Western Airborne Contaminants Assessment Project

Quality Assurance Project Plan


Oldman Lake
Glacier National Park

May 2004

Marilyn Morrison Erway
Staci Simonich
Donald Campbell
Adam Schwindt
Linda Geiser
Kimberly Hageman
David Schmedding
Glenn Wilson
Sascha Usenko
Luke Ackerman
Scott Echols
Dixon Landers

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QUALITY ASSURANCE PROJECT PLAN

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Marilyn Morrison Erway
Dynamac Corporation
c/o U.S. EPA Western Ecology Division
Corvallis, OR

Staci Simonich
Dept. of Env. and Molecular Toxicology
Oregon State University
Corvallis, OR

Donald Campbell
U.S. Geological Survey
Denver, CO

Adam Schwindt
Dept. of Microbiology
Oregon State University
Corvallis, OR

Linda Geiser
USDA-Forest Service
Siuslaw National Forest
Corvallis, OR

Kimberly Hageman
David Schmedding
Glenn Wilson
Sascha Usenko
Luke Ackerman
Dept. of Env. and Molecular Toxicology
Oregon State University
Corvallis, OR

Scott Echols
Dynamac Corporation
c/o U.S. EPA Western Ecology Division
Corvallis, OR

Dixon Landers
U.S. Environmental Protection Agency,
NHEERL-Western Ecology Division,
Corvallis, OR

WESTERN AIRBORNE CONTAMINANTS ASSESSMENT PROJECT

Management Approvals:
Signature indicates that this QAPP is approved and will be implemented in conducting the research of this project.

Roger Blair
USEPA, Branch Chief
Aquatic Monitoring and
Bioassessment Branch

Signature 6/19/04 *Date*

Dixon Landers
USEPA, Project Leader

Signature 08 Jun 04 *Date*

Tamara Blett
National Park Service
Project Coordinator

Signature 15 June 04 *Date*

Principal Investigators:

Staci Simonich
OSU Dept. of Environmental and
Molecular Toxicology

Signature 6/15/04 *Date*

Donald Campbell
USGS, Denver

Signature 6/13/04 *Date*

Michael Kent
OSU Dept. of Microbiology

Signature 6/15 *Date*

Carl Schreck
Oregon Cooperative Fish and
Wildlife Research Unit

Signature 6/15/04 *Date*

WESTERN AIRBORNE CONTAMINANTS ASSESSMENT PROJECT

Principal Investigators (continued):

Linda Geiser
USDA- Forest Service
Signature Date 6/13/04

Howard Taylor
USGS, Boulder
Signature Date 6/15/04

Marilyn Morrison Erway
Dynamac Corp., WED
Signature Date 15 June 04

Quality Assurance:

Signature indicates that this QAPP meets the quality requirements of WED.

Robert Ozretich
Quality Assurance Officer
Signature Date 9 June 04

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ABBREVIATIONS AND ACRONYMS

AR	matrix spike
ARD	Air Resources Division, National Park Service
ASE	accelerated solvent extraction
BDL	below detection limit
CIC	constant input concentration
CPO	Cheeka Peak Observatory, Neah Bay, WA
CRS	constant rate of supply
DENA	Denali National Park
DL	detection limit
DOC	dissolved organic carbon
ECNI	electron capture negative ionization
EDL	estimated detection limit
EI	electron impact
ELISA	enzyme-linked immunosorbant assay
EMAP-SW	Environmental Monitoring and Assessment Program- Surface Water component
EMERGE	European Mountain lake Ecosystems: Regionalisation, diagnostics & socio-economic Evaluation
EROD	7-ethoxyresorufin-O-deethylase
FB	field blank
FFP	flag field precision
FIP	flag instrument precision
FLB	flag laboratory blank
FP	field precision
GAAR	Gates of the Arctic National Park and Preserve
GC	gas chromatograph
GC/MS	gas chromatographic mass spectrometry
GLAC	Glacier National Park
GPC	gel permeation chromatography
GPS	global positioning system

HCH	hexachlorocyclohexanes
HM	heavy metals
IC	instrument calibration
ICP-AES	inductively coupled plasma- atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
IP	instrument precision
IMPROVE	Interagency Monitoring of Protected Visual Environments
LB	laboratory blank
LP	laboratory precision
MA	macrophage aggregate
MDL	method detection limit
MORA	Mount Rainier National Park
NADP	National Atmospheric Deposition Program
NCI	negative chemical ionization
NF	National Forest
NHEERL	National Health and Environmental Effects Research Laboratory, USEPA
NIST	National Institute of Standards and Technology
NMHC	non-methane hydrocarbons
NOAT	Noatak National Preserve
NPS	National Park Service
NRP	National Research Program
OC	organic compound
OLYM	Olympic National Park
OSU	Oregon State University
PAH	polycyclic aromatic hydrocarbon
PAN	peroxyacetyl nitrate
PBDE	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
PIs	principal investigators
PNW	Pacific Northwest
POPs	persistent organic pollutants

PS	instrument performance standard
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RFS	routine field sample
RIA	radioimmunoassay
RM	reference material
RMS	Rocky Mountain Snowpack
ROMO	Rocky Mountain National Park
RPD	relative percent difference
RSD	relative standard deviation
SCPs	Spheroidal Carbonaceous Particles
SEC	Simonich Environmental Chemistry (Laboratory)
SEKI	Sequoia/Kings Canyon National Park
SOCs	semi-volatile organic compounds
SR	surrogate spike
SRM	standard reference material
SWE	snow water equivalence
TBD	to be determined
UMN	University of Minnesota
UMNRAL	University of Minnesota Research Analytical Laboratory
USDA	United States Dept. of Agriculture
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USGS-BRD	United States Geological Survey- Biological Resource Division
VOC	volatile organic compound
WACAP	Western Airborne Contaminants Assessment Program
WBC	white blood cells
WED	Western Ecology Division, NHEERL, USEPA, Corvallis, OR
WRS	Willamette Research Station (Corvallis EPA Analytical Laboratory)

A. PROJECT MANAGEMENT

1.0 Introduction

1.1 Introduction

The Western Airborne Contaminants Assessment Project (WACAP) is being designed and implemented by the National Park Service's Air Resources Division, in cooperation with many western Parks, to provide spatially extensive, site specific, and temporally resolved information regarding the exposure, accumulation, and impacts of airborne contaminants in these ecosystems. WACAP is designed as a five-year program, with the first year for pilot work and method development, years two through four for sample collection and analyses, and year five for data analyses and publications. The purpose of this effort is to establish the degree of risk that western national parks may be experiencing from the long-range transport of airborne contaminants.

The contaminants of interest are a broad range of compounds and elements that are sometimes called Persistent Bioaccumulative Toxics or PBTs. This group contains a variety of semi-volatile organic compounds (SOCs) and persistent organic pollutants (POPs) such as PCB (polychlorinated biphenyl), DDT, and HCH (hexachlorocyclohexanes) as well as elements such as mercury. These materials are direct or indirect products of human industrial activity and can be transported thousands of miles in the atmosphere either in the gas phase or as fine particles. In some cases they can be deposited to aquatic or terrestrial ecosystems and then be volatilized and transported further until they reach another area where the conditions are right for deposition to occur again, through wet deposition (i.e., rain or snow), dry deposition, and sorption to natural vegetation (Simonich and Hites, 1994b; Simonich and Hites, 1994a). These semi-volatile constituents have the potential to preferentially accumulate in high latitude and high elevation ecosystems, due to global distillation and regional cold condensation (Simonich and Hites, 1995a; Wania and Mackay, 1996; Blais et al., 1998). For these reasons, sensitive high elevation ecosystems in our National Parks have the potential to be impacted by these air toxics.

Eight National Parks will participate in WACAP: Sequoia, Rocky Mountain, Olympic, Mt. Rainier, Glacier, Denali, Noatak, and Gates of the Arctic. Two lake catchments have been selected in most of these Parks (Noatak and Gates of the Arctic each have one site), for a total of 14 sites. The eight Parks represent a latitudinal (north-south) as well as coastal versus interior (east-west) gradient.

WACAP will sample a variety of ecosystem indicators to provide information about contaminant accumulation. These indicators include:

- Snow, to measure direct atmospheric loading;
- Fish, to measure food web impacts and bioaccumulation;
- Water, to measure hydrophilic current-use chemicals;
- Lake sediments, to provide information about historic trends of contaminant loading to watersheds;
- Lichens, to measure food web impacts and bioaccumulation;

- Willow bark, to measure ecosystem exposure; and
- Moose meat, to sample subsistence food items (other than fish) in Alaska parks.

Snow will be sampled at each site each year for three years, while the other indicators will be sampled once during the project.

Each ecosystem indicator will be analyzed for up to four types of analytes (see Table 1.1):

- Semi-volatile organic compounds (SOCS), including persistent organic pollutants (POPs) such as PCB, DDT, and HCH, and current-use chemicals;
- Mercury
- Metals (primarily cadmium, copper, lead, nickel, vanadium, and zinc)
- Major ions and nutrients

In addition, some ecosystem indicators will measure analytes specific to their indicator:

- Snow: total particulate C and N in snow
- Fish: condition factors of fish (e.g., weight, length), hematology, histology
- Lake sediment: dating profiles, spherical carbonaceous particle analysis, percent moisture, and ash-free dry weight

Three National Parks in the Pacific Northwest region (Olympic, Mt. Rainier, and North Cascades) will participate in additional snow sampling. This area of the U.S. is likely the most frequent recipient of Asian trans-Pacific air masses, and the addition of more intense snow sampling will provide more information about precipitation chemistry in these areas. The purpose of the additional snow sampling will be to 1) determine the seasonal flux, and spatial and temporal variability in semi-volatile organic compounds attributable to snow deposition; and 2) investigate probable sources of these pollutants by linking this work with back-trajectory modeling, and direct sampling of trans-Pacific air masses. Approximately thirteen additional sites will be sampled over three years in these three Parks. A bulk precipitation collector will be used in Olympic National Park because rain-on-snow events are likely to occur there; this collector will provide information on temporal rather than spatial variability. The additional snow sampling will begin in Spring 2004 and continue through 2007.

Each ecosystem indicator has a lead researcher who is responsible for developing the QA section for that indicator. QA objectives for each major analyte type are listed in Section 2.0, then there is a section for each ecosystem indicator that includes protocols for sample collection, sample custody (shipping, storage, holding times), sample processing, and sample analysis. QA Plans for additional WACAP laboratories are included in the appendices. Quality control procedures are specified, as well as data quality evaluation procedures including collection of field duplicates.

Table 1.1 Contaminants selected for inclusion in WACAP

POPs (9 of 12 Priority POPs)	Current-Use Chemicals	Heavy metals (total values)
Hexachlorobenzene (HCB)	polybrominated diphenyl ethers	Cadmium
Hexachlorocyclohexanes (HCH) (Lindane)	Triazine Herbicides (Atrazine, etc.) and degradation products	Copper
Chlordanes	Organophosphorus Pesticides (chlorpyrifos, diazinon, malathion, etc.) and degradation products	Lead
Nonachlors	Dacthal (DCPA)	Mercury
Heptachlors	Trifluralin	Nickel
DDTs/DDEs	Chloroacetanilide Herbicides (Metolachlor, Acetochlor, etc.)	Vanadium
Dieldrin	Thiocarbamate Herbicides (EPTC (Eptam), Pebulate), fluorinated organic compounds	Zinc
Endosulfan		
PCBs		
PAHs		
Note: Toxaphene, and Polychlorinated dibenzo-*p*-dioxins and furans are not included		

WACAP has some difficult QA issues to work with. The total number of sites is relatively small (14), and spread over a wide geographic area that will probably require multiple sampling teams. Most of the sites are very remote, so it will be important to maintain sample integrity during transport and storage. Sampling will occur over a three year time period, with only one indicator (snow) being sampled annually, so there will be both site-to-site comparability issues as well as year-to-year comparability issues for the same site. We will have to make critical choices to maximize the use of project resources and establish in advance the information needed to evaluate data quality.

WACAP has three main laboratories (Simonich Environmental Chemistry Laboratory, WRS Analytical Laboratory, and the USGS Boulder Laboratory), with up to four additional laboratories providing particular analyses on an indicator (e.g., dating profile for sediments, or nitrogen and sulfur analyses on lichens). In some cases, e.g., metals analyses for snow samples, the laboratories have been routinely analyzing for previous and/or ongoing projects. In other cases, e.g., SOC analyses in all indicators, the laboratory is developing new methods specifically for WACAP. We have tried to maintain consistency by having the same laboratory analyze all indicators for the same analyte type, where possible.

Quality assurance uses both quality assessment and quality control (QC). Quality assessment evaluates data quality as samples are being measured with performance evaluation samples, while QC is used to control the analytical processes before and during sample analysis to minimize data loss through out-of-control analytical systems. WACAP will be using both, but because of the high costs of collecting samples, QC will be important so corrective actions can be initiated and data loss minimized.

1.2 Goals

The goal of WACAP is to assess the deposition of airborne contaminants in eight western National Parks, providing regional and local information on exposure, accumulation, impacts, and probable sources. Detailed background information and the approach developed for WACAP are described in the WACAP Research Plan (Landers et al., 2003).

1.3 Personnel

WACAP will be an integrated team effort, including not only scientists from a variety of institutions but also resource experts and specialists from each of the participating National Parks. Each sample type (matrix) has a Principal Investigator (PI) who will be responsible for the sampling and analysis methods for that media. Table 1.2 lists the WACAP Science Team.

Table 1.2 WACAP Science Team

Name and Affiliation	Responsibilities	Email
Tamara Blett NPS-Air Resources Division 12795 W. Alameda Parkway Lakewood, CO 80228	Project coordination	Tamara_Blett@nps.gov
Donald H. Campbell* **George P. Ingersoll** **M. Alisa Mast** U.S. Geological Survey MS 415 Denver Federal Center Denver, CO 80225	Snow Analyses	dhcampbe@usgs.gov
Marilyn Morrison Erway Dynamac Corp. c/o U.S.EPA, NHEERL Western Ecology Division 200 SW 35th St., Corvallis, OR 97333	Quality assurance, data base development, within project coordination, logistics	Erway.Marilyn@epa.gov
Linda Geiser* USDA-FS, PNW Region Air Resource Management Program P.O. Box 1148 Corvallis, OR 97339 **Peter Neitlich**, NPS, Forest Inventory and Analysis Program	Lichens	lgeiser@fs.fed.us
Dan Jaffe* University of Washington-Bothell 18115 Campus Way NE Bothell, WA 98011 **Lyatt Jaegle** Dept. of Atm.Sciences, U. of Washington Seattle, WA	Atmospheric Analysis	djaffe@u.washington.edu
Mike Kent Dept. of Microbiology Oregon State Univ., Corvallis, OR 97331 **Carl Schreck** Oregon Cooperative Fish and Wildlife Research Unit, USGS-BRD 104 Nash Hall Oregon State Univ., Corvallis, OR 97331	Fish sampling and analyses	Michael.Kent@orst.edu Carl.Schreck@orst.edu
Dixon Landers U.S. EPA, NHEERL Western Ecology Division 200 SW 35th Street Corvallis, OR 97333	Project Director Lake sediment sampling	Landers.Dixon@epa.gov
Staci Simonich Dept. of Env. and Molecular Toxicology Dept. of Chemistry 1141 Ag and Life Sciences Oregon State Univ., Corvallis, OR 97331	Organic Analyses Metal Analyses, Willow bark, and subsistence foods sampling	staci.simonich@orst.edu
Howard E. Taylor USGS, 3215 Marine St., Suite E-127 Boulder, CO 80303	Metal Analyses	hetaylor@usgs.gov

2.0 Data Quality Objectives

The WACAP data quality objective is to obtain data to assess the deposition of airborne contaminants at 14 sites in eight western national parks by determining if SOCs, mercury, and metals are present, and if present, determine where they are accumulating, geographically and by elevation. WACAP will follow a standard QA approach of establishing QA objectives, then specifying how data quality will be controlled and assessed. This approach will include:

- Selecting methods and sample processing procedures with detection limits low enough to detect the contaminants and measure other metrics of interest;
- Establishing sampling protocols that will be consistent and standardized at all sites each year and among all sampling participants;
- Selecting shipping, storage, and processing methods to maintain sample integrity until analysis and minimize contamination;
- Establishing quality control (QC) procedures to monitor performance and calibration of measurement systems and provide rapid feedback so corrective actions can be taken before affecting data quality;
- Establishing methods to assess data quality, e.g., collection of duplicates to estimate precision and analysis of performance evaluation samples to estimate accuracy;
- Preparing a database with procedures to verify and validate data and document data quality.

QA objectives are established for measurements based on the data quality required to meet project objectives. For example, data collected for WACAP will be used to report information about ecosystem indicators, and will not be used to detect trends in contaminants. Objectives are described and measured by indicators of data quality, with the most common being precision and accuracy. If the precision and accuracy of data collected for WACAP are equal to or less than the objectives listed here, then we know we can use these data to meet our project objectives. If precision and accuracy are greater than our objectives, we will flag the data and then evaluate each case before the data are used. These indicators and the samples used to measure them are described below:

- Precision is the "degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions" (Taylor, 1987). Precision indicates variability, and is estimated in terms of the standard deviation of duplicates or replicates. It can be estimated at different points in the sampling process, e.g., in the field during sample collection by collecting field duplicates, in the laboratory during sample processing, and in the laboratory during analysis. WACAP will collect a limited number of field duplicates in some matrices, such as snow and sediment, due to sampling constraints, so precision will be estimated primarily with analytical duplicates.
- Accuracy indicates the degree of agreement between a measured and true value of a reference sample, and is estimated in terms of difference from the reference value. Accuracy is usually assessed during sample analysis. Bias is a systematic error in the measurement process, and can be caused by any number of factors, such as contamination, calibration errors, temperature effects, or extraction inefficiencies (Taylor, 1987). Bias is controlled by using procedures in the field and laboratory that will control

and reduce these effects, e.g., QC calibration checks, monitoring storage temperatures, extraction spikes.

- Method detection limit (MDL) is the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (Glaser et al., 1981). Detection limits are assessed at the analytical level, and are an important characteristic of the measurement process, especially when comparing data from different time periods.
- Contamination is the influence of non-sample sources of the analytes of interest. Contamination can occur at multiple points during the sampling process, e.g., from containers, handling, and storage. The lower the concentration levels of the analytes of interest, the more critical it becomes to prevent contamination. Blanks at various points in the sampling process are used to measure contamination.
- Percent recovery is a measure of the efficiency of the extraction procedure. Recovery is assessed with the use of analytical spikes during the extraction procedure.
- Completeness is the amount of valid data actually obtained that is required to achieve the project objectives. For example, if only one year of snow sampling data is collected from a site instead of three years, will we still be able to meet the project objective of using snow as a measure of direct atmospheric loading?
- Representativeness is the degree to which data truly represent a characteristic of a population or environmental condition.
- Comparability is the degree of confidence with which two or more datasets may be compared. Datasets with similar precision, accuracy, and detection limits and little bias will be comparable.

Data comparability both within WACAP and outside WACAP will be an important issue to think about when deciding how much information about data quality will be needed. Data from most of the ecosystem indicators will be collected one time at each site, so we will want the data to be comparable among the sites over the three year time period, i.e., we will want to compare information from each site, even though the information will have been collected in different years. This information will be used to describe spatial patterns in contaminants, so we want to be sure that any differences are true differences in ecosystem indicators, and not due to differences in collection or data analysis from year to year. Estimating variability each year will give some idea of the normal variability in these ecosystem indicators. Variability in data analysis can be controlled and evaluated within the laboratory, but variability in ecosystem indicators, field conditions, and collection processes will need to be estimated by collecting field duplicates. Field duplicates add extra samples at every step, so careful consideration needs to be given to how many we need.

WACAP QA objectives are established at each laboratory, based on the criteria used by the laboratory and required to meet WACAP goals. For some WACAP analytes, the precision and accuracy objectives use an absolute value for lower concentration ranges, and a relative value at higher concentration ranges, thus reducing the problem of unreasonable objectives for low analyte concentrations. A concentration range is specified for each variable to determine whether the absolute or the relative term applies.

The precision objective is based on the standard deviation (s) for the absolute term at the lower concentrations, and the percent relative standard deviation (%RSD) for the relative term at the higher concentrations:

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{(n-1)}} \qquad \%RSD = \frac{s}{\bar{x}} \times 100$$

where x_i is an individual measurement, and $\bar{X}$ is the mean of the set of measurements.

Relative percent difference (%RPD) can also be used to estimate precision with the following calculation:

$\%RPD = \frac{|x_1 - x_2|}{\bar{x}} \times 100$ where x_1 and x_2 are individual measurements, and $\bar{x}$ is the mean value of the two measurements. When objectives are based on %RSD but measured in %RPD (or vice versa), the equivalent value can be calculated from the relationship:

$$\%RPD = \%RSD \times \sqrt{2}$$

For accuracy, the objective is based on the difference between the measured and target value of a sample in the lower concentration range, and as the percent difference in the higher concentration range. For repeated measurements of the same sample, the net bias is calculated by the difference between the mean of the repeated measurements and the target value in the lower concentration range, and by the percent difference between the mean and the target values in the higher concentration range.

Stable isotope labeled surrogate compounds will be added to all field samples prior to the extraction step for organic analyses to assess the recovery of every extraction. Percent recovery will be calculated with the following calculation:

$\%recovery = \frac{C_m}{C_i} \times 100$, where C_m is the measured concentration of the surrogate in the sample, and C_i is the initial concentration of the surrogate spike.

2.1 Quality Assurance Objectives for Semi-Volatile Organic Compounds

The SOCs, including POPs and current-use chemicals, that will be analyzed in snow, fish, vegetation, lake water, sediment, and subsistence native foods are listed in Table 1.1. Concentration ranges of SOCs in high elevation ecosystems, in different matrices, that may be similar to what we find in our WACAP sites are provided in Table 2.1.1. QA objectives for SOC analyses are summarized in Table 2.1.2 and described below.

Table 2.1.1 Summary of SOC concentrations measured in high elevation ecosystems

Matrix	Study Location	SOCs measured	*Reference*	Concentration Range
Snow	European Alps	PCBs (sum of seven congeners)	1	0.20 – 2.2 ng/L
		HCH (sum of α and γ)	1	0.022 – 1.1 ng/L
		DDTs	1	0.073 –0.330 ng/L
		PAHs (sum of 22 PAHs)	1	5.6 – 81 ng/L
	Canadian Rockies	PCBs	6	1.1 – 1.4 ng/L
		HCHs	6	0.17 – 0.43 ng/L
	Sierra Nevada Mountains, CA	Trifluralin	8	<0.1 – 2.4 ng/L
		Chlorothalonil	8	<0.57 – 13 ng/L
		Chlorpyrifos	8	0.3 – 13 ng/L
		Diazinon	8	<0.057 – 14 ng/L
		Malathion	8	<0.045 – 18 ng/L
		HCHs (sum of α and γ)	8	<0.018 – 9.4 ng/L
		Endosulfans (sum of I and II)	8	<0.035 – 3.46 ng/L
Fish	European Alps	HCB	2	0.053 – 1.6 ng/g wet weight
		PCBs	2	0.17 – 26.6 ng/g wet weight
		HCHs	2	0.10 – 3.2 ng/g wet weight
		DDTs	2	0.25 – 65 ng/g wet weight
Sediment	European Alps	HCB	2	12 – 410 pg/cm^2 wet weight
		PCBs	2	59.2 – 493 pg/cm^2 wet weight
		PAHs (sum of 10 PAHs)	3	180 – 1100 ng/g dry weight
Lake Water	European Alps	PAHs (sum of 6 PAHs)	4	0.7 – 1.1 ng/L
		PCBs (sum of 7 PCBs)	5	0.026 – 0.11 ng/L
		DDT (sum of p,p'-DDT and p,p'-DDE)	5	0.001 – 0.016 ng/L

Matrix	**Study Location**	**SOCs measured**	*Reference*	**Concentration Range**
Lake Water	European Alps	HCB	5	0.004 – 0.008 ng/L
		HCHs (sum of α and γ)	5	0.3 – 2.9 ng/L
		Endosulfans (sum of I, II, and sulfate)	5	0.12 – 1.1 ng/L
	Sierra Nevada Mountains	Trifluralin	9	1.2 – 108.12 ng/L
		Diazinon	9	0.92 – 74.1 ng/L
		Chlorothalonil	9	1.94 – 6.62 ng/L
		Chlorpyrifos (sum of parent and oxon)	9	113 – 161.6 ng/L
		Malathion	9	65 – 83 ng/L
		Endosulfans (sum of I and II)	9	105 – 165 ng/L
Conifer Needles	Canadian Rockies	HCHs	7	0.043 – 2.43 ng/g dry weight
		PCBs	7	0.055 – 17.5 ng/g dry weight
		Endosulfans	7	0.011 – 2.93 ng/g dry weight

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Table 2.1.2 Quality Assurance Objectives for SOC Analyses

Sample Type	Units	Precision Objective	Accuracy Objective
replicate instrument injections	ng/L or ng/g	25% RPD[1]	
field replicate samples	ng/L or ng/g	100% RPD[1]	
surrogate spike	ng/L or ng/g		30% < %recovery < 130%
standard reference material	ng/L or ng/g		Within vendor's acceptance window

[1]relative percent difference

Precision will be estimated by the analysis of co-located field duplicates and analytical duplicates. Field duplicates represent both the analytical precision and the spatial variability at the site. The goal for collection of field duplicates for lake water, fish, and vegetation samples is to collect at least one field duplicate per Park during the project. See Table 4.1 for the schedule for collection of field duplicates for snow. Analytical duplicates are replicate instrument injections that will be analyzed at a frequency of least 10%.

Accuracy will be assessed from the recoveries of isotopically labeled surrogates spiked into each individual field sample, and from the analysis of Standard Reference Materials (SRMs). A known amount of the surrogate spike will be added directly to every field sample and blank prior to the extraction procedure to assess the recovery of every extraction. The acceptance criteria for surrogate recoveries relative to the internal standard must be between 30 and 130%. Compounds in violation of the recovery criteria will be flagged.

Additionally, SRMs from the National Institute of Standards and Technology (NIST) will be analyzed for WACAP matrices for which matrix relevant reference materials are available. These SRMs include: SRM 1944 (New York/New Jersey Waterway Sediment) and SRM 1946 (Lake Superior Fish) (or SRM 1588a (Organics in Cod Liver Oil) if SRM 1946 is not in stock). In the event that the target PCB or PAH analyte levels are much lower than those in SRM 1944, then Environment Canada EC-5 reference material will be used. If additional SRMs for relevant matrices, including SRMs for the analysis of current-use pesticides, become available, these SRMs will also be incorporated into the analysis. Accuracy will be evaluated by determining whether the concentrations measured in the SRM are within the vendor's required acceptance windows. Values outside the acceptance windows will be justification for reanalysis of the SRM.

Detectability refers to the determination of the low-range critical value of a characteristic that a method specific procedure can reliably discern. A MDL study will be completed during

method validation (see section 12.3) using a typical matrix sample. It is necessary that all sample processing steps of the analytical method are included in the determination of the MDL.

The MDLs for each target analyte will be the instrument detection limits attenuated by individual matrix impacts. The instrument detection limits are ~ 0.1ng/µL to 0.01ng/µL for those compounds analyzed by electron impact (EI) ionization MS and ~ 0.1ng/µL to 0.001ng/µL for those analyzed by negative chemical ionization (NCI) MS. The matrix impacts are expected to reduce sensitivity by up to an order of magnitude but will be very dependent on the individual matrix. The expected MDLs for the analytical methods and matrices used in WACAP are estimated in Table 2.1.3.

2.2 Quality Assurance Objectives for Trace Metals Analyses

Trace metals will be analyzed in snow, fish, lichen, sediment, and moose meat at the USGS National Research Program Laboratory in Boulder, CO by ICP-MS. The priority metals for WACAP are Cd, Cu, Pb, Ni, V, and Zn. Expected concentrations ranges for the priority metals are listed in Table 2.2.1. Quality assurance objectives for these metals are listed in Table 2.2.2, and are based on the sample concentration range. Instrument detection limits for these metals are listed in Table 2.2.3. Examples of potential detection limits for trace metals in sample digests are provided in Table 2.2.4, using examples of sample quantities and final volumes.

2.3 Quality Assurance Objectives for Mercury Analyses

Snow samples will be analyzed for mercury at the USGS Wisconsin Mercury Lab by oxidation, purge and trap, cold vapor atomic fluorescence spectrometry. Expected concentration ranges are listed in Table 2.3.1. The detection limit is 0.4 ng/L. Other sample matrices will be analyzed for mercury at the WRS Analytical Laboratory by direct analysis with a Milestone DMA-80 with a detection limit of 0.05 ng. QA objectives for mercury analyses are listed in Table 2.3.2.

Table 2.1.3 Expected SOC Method Detection Limits (MDLs) (approximate) for all WACAP Target SOC analytes

Sample Matrix	Units	Expected MDL
Snow and Lake Water	ng/L	0.01 – 1
Fish, Sediment, and Vegetation	ng/g wet weight	0.01 – 1

Table 2.2.1 Expected concentrations ranges for metals

Analyte	Lichens µg/g dry	Snow µg/L	Sediment µg/g dry	Fish liver µg/g dry	Fish fillet µg/g dry	Meat µg/g dry
Cd	0.01 - 0.5	0.01 - 0.5	5 - 50	0.1 – 5	0.01 - 0.5	0.01 - 1
Cu	0.01 - 1	0.005 - 0.5	5 - 50	0.1 – 5	0.01 - 0.5	0.01 - 1
Pb	0.01 - 0.5	0.05 - 1	10 - 500	0.1 - 20	0.01 - 1	1 - 30
Ni	0.1 - 10	0.01 - 0.5	1 - 500	0.5 - 20	0.1 - 1	0.1 - 10
V	0.1 - 10	0.005 - 0.05	10 - 100	1 – 50	0.1 - 5	0.1 - 10
Zn	1 - 100	0.1 - 5	50 - 500	0.5 - 300	5 - 50	20 - 100

Table 2.2.2 Quality Assurance Objectives for Trace Metals Analyses

Units	Concentration Range	Precision Objective	Accuracy Objective
µg/L	≤ 10 times detection limit	85% RSD	85% difference
	> 10 times detection limit	15% RSD	15% difference

RSD = relative standard deviation

Table 2.2.3 Trace metals and detection limits

Analyte	Units	Detection Limit
Cd	µg/L	< 0.002
Cu	µg/L	< 0.04
Pb	µg/L	< 0.004
Ni	µg/L	< 0.02
V	µg/L	<0.007
Zn	µg/L	< 0.04

Table 2.2.4 Examples of potential detection limits for trace metals in sample digests, using given sample quantities and final volumes. Actual detection limits will vary with final sample weights and digest volumes.

Sample Matrix:	Lichens	Snow	Sediment	Fish liver	Fish fillet	Meat
Digestion Quantities:	0.1 g/ 50 ml	na	0.1 g/ 1000 ml	0.1 g/ 50 ml	0.1 g/ 50 ml	0.1 g/ 50 ml
Units	µg/g	µg/L	µg/g	µg/g	µg/g	µg/g
Analyte:						
Cd	0.001	< 0.002	0.02	0.001	0.001	0.001
Cu	0.02	<0.04	0.4	0.02	0.02	0.02
Pb	0.002	< 0.004	0.04	0.002	0.002	0.002
Ni	0.01	<0.02	0.2	0.01	0.01	0.01
V	0.004	<0.007	0.07	0.004	0.004	0.004
Zn	0.02	<0.04	0.4	0.02	0.02	0.02

Table 2.3.1 Expected Concentrations of Mercury

Matrix	Units	Concentration Range
Snow	ng/L	0.5-5
Fish liver	ng/g	1-100
Fish filet	ng/g	1-100
Sediment	ng/g	1-500
Lichen	ng/g	0.5-10
Meat	ng/g	1-50

Table 2.3.2 Quality Assurance Objectives for Mercury Analyses

Units	Concentration Range	Precision Objective	Accuracy Objective
µg/L	≤ 15	± 2 s.d.	± 2
	> 15	15% RSD	10% difference

s.d. = standard deviation
RSD = relative standard deviation

2.4 Quality Assurance Objectives for Major Ion Analyses

Quality assurance objectives and expected concentration ranges for major ion analyses in lake water are listed in Table 2.4.1.

Table 2.4.1 Quality Assurance Objectives for Major Ion Analyses

Analyte	Units	Expected Sample Concentration Range	Concentration	Precision Objective[2]	Accuracy Objective[3]
Temperature	degrees C	5 to 30	all	5%	NA
Conductivity	µS/cm	1 to 100	≤ 40 > 40	± 2 3%	± 2 5%
Dissolved oxygen (DO)	mg/L; % saturation	50 to 100	all	10%	10%
Chlorophyll *a*	µg/L	2 to 20	all	20%	20%
Turbidity	NTU	0.1 to 50	≤ 10 > 10	± 2 10%	± 1 10%
pH	pH units	4.0 to 7.5	≤ 5.75 >5.75	±0.07 ± 0.15	± 0.05 ± 0.10
Acid Neutralizing Capacity (ANC)	µeq/L	-100 to 500	≤ 100 > 100	± 5 5%	± 4 4%
Nitrate (NO_3)	mg N/L	0.03 to 10	≤ 0.4 > 0.4	± 0.03 5%	± 0.02 5%
Ammonium (NH_4)	mg N/L	0.02 to 5	≤ 0.4 > 0.4	± 0.03 5%	± 0.02 5%
Dissolved Organic Carbon (DOC)	mg C/L	0.1 to 15	≤ 1 > 1	± 0.1 10%	± 0.1 7%
Dissolved Inorganic Carbon (DIC)	mg C/L	0.1 to 25	≤ 1 > 1	± 0.1 10%	± 0.1 7%
Total Dissolved Nitrogen (TDN)	mg N/L	0.1 to 10	≤ 0.3 > 0.3	± 0.05 10%	± 0.02 7%
Total Dissolved Phosphorous (TDP)	mg P/L	0.1 to 100	≤ 0.3 > 0.3	± 0.05 10%	± 0.02 7%
Sulfate (SO_4)	mg SO_4/L	0.05 to20	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Chloride (Cl)	mg Cl/L	0.03 to 50	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Calcium (Ca)	mg Ca/L	0.02 to 50	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Magnesium (Mg)	mg Mg/L	0.01 to 10	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Sodium (Na)	mg Na/L	0.02 to 50	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%
Potassium (K)	mg K/L	0.04 to 5	≤ 1.5 > 1.5	± 0.10 5%	± 0.10 5%

[2]Precision is estimated as the standard deviation of repeated measurement at the lower concentration range, and as percent relative standard deviation at the higher concentration range.

[3] Accuracy is estimated as the difference between the measured and target values of performance evaluation samples at the lower concentration range, and as the percent difference at the higher concentration range.

B. MEASUREMENT/DATA ACQUISITION

3.0 Statistical Research Design

3.1 Sampling Strategy

Site Selection

We selected one to two catchments (i.e. sites) within each of the participating National Parks that met pre-established criteria:

- Small catchment typical of the types of catchments found in the park in question (elevation, soils, vegetation, aspect, etc.)
- Catchment contains a lake ($\geq$ 5 m deep; larger than ~0.8 hectares in surface area)
- Lake should contain reproducing fish population (preferably salmonids)
- No anadromous fish reach the lake
- Lake should be without major inlets or outlets, or glaciers in the catchment
- Lake bathymetry is acceptable for sediment core analysis
- Safe access is possible by available means in late spring and summer
- Gill netting of fish is acceptable
- Catchments are located within the seasonally "permanent" snow pack development for the Park
- Both catchments located in the same general quadrant within the Park

There is large variability among candidate catchments within and among parks. Given the large geographic scale of WACAP, several major ecological regions were included in the final selection. We were initially interested in selecting sites within each Park that differed by 1000 m or more in elevation in order to examine elevational gradients and their influence on contaminants. Finding sites with this elevational difference was simply not possible once we began examining catchments meeting our criteria. We also sought to choose catchments that were generally in the same airshed, whether or not they differed significantly in elevation. Therefore, candidate sites were discussed with Dr. Jaffe (WACAP atmospheric science lead) prior to final selection to ensure that atmospheric transport issues would likely not be problematic. The two exceptions to this strategy are in Rocky Mountain NP and Glacier NP where the selected lakes are at almost the same elevation but on opposite sides of the continental divide.

In our final selections of catchments in each Park, the catchments selected represent "elevation duplicates" in the sense that they are located at approximately the same elevation. In Glacier National Park we were able to find two lakes separated by several hundred meters in elevation but that is the only case. The sites in northern Alaska are in two National Parks or Preserves, with one site in Noatak National Preserve and one site in Gates of the Arctic National Park and Preserve. Two of the three sites identified in Denali National Park (McLeod and

Foraker) are tentative, and only one of these sites will be selected after information about the fish populations in these lakes is collected in the summer of 2003. Table 3.1.1 summarizes the attributes of the selected catchments/lakes for each Park.

Table 3.1.1 Lake catchments for WACAP

Park	Lake Name	Elevation (m)	Fish Species	Latitude (dec.)	Longitude (dec.)
Noatak	Burial	427	lake trout	68.43	159.18
Gates of the Arctic	Matcharak	488	lake trout	67.75	156.21
Denali	Wonder	610	lake trout, burbot, arctic char, arctic grayling	63.48	150.88
Denali	McLeod	609	unknown	63.38	151.07
Denali	Foraker	732	unknown	63.22	151.60
Glacier	Oldman	2026	cutthroat trout	48.50	113.46
Glacier	Synder	1600	westslope cutthroat trout	48.62	113.79
Olympic	PJ Lake	1433	brook trout	47.95	123.42
Olympic	Hoh Lake	1384	brook trout	47.90	123.79
Mt. Rainier	Unnamed LP19	1372	rainbow trout	46.82	121.89
Mt. Rainier	Golden	1372	rainbow trout	46.89	121.90
Rocky Mt.	Mills	3030	rainbow trout	40.29	105.64
Rocky Mt.	Lone Pine	3024	brook trout	40.22	105.73
Sequoia	Emerald	2800	brook trout	36.58	118.67
Sequoia	Pear	2904	brook trout	36.60	118.67

Indicators and Contaminants

There are a wide variety of possible indicators that could be used to provide information regarding the level to which airborne contaminants have become entrained in National Park ecosystems. Similarly, there is a large selection of contaminants that could be measured. One of the early WACAP design tasks was to winnow the expansive list of possible indicators as well as contaminants down to a manageable and affordable number. In doing this, we frequently referred back to the objective of the WACAP program to insure that indicators that we selected fulfilled, collectively, broad and in some cases, multiple, purposes. Moreover, a secondary concern was to select indicators that would compare to other similar ongoing and historic studies (e.g., the EMERGE program, European Mountain lake Ecosystems: Regionalisation, diaGnostics, and socio-economic Evaluation) regarding contaminant impacts in remote alpine and arctic locations.

There are three classes of contaminants in which we are especially interested: POPs, current-use chemicals, and heavy metals. Table 1.1.1 lists those analytes we will measure under each of these general headings. Again, choices had to be made which maximized our ability to determine the presence of the most likely contaminants while avoiding those that were extremely expensive to analyze. If there were conflicts in collection methods between these contaminants, i.e., sampling utensils, containers, etc., we selected our choices on the priority of SOC and Hg analyses over metals analyses.

Table 3.1.2 summarizes the sampling and analysis procedures for each indicator selected for WACAP (snow, fish, lichens, willow bark, subsistence native food, water, and lake sediment). More detailed information about each indicator is provided in the specific section for each indicator, including sample collection protocols, and sample processing and analysis procedures.

3.2 Analytical Laboratories

Table 3.2.1 summarizes the analytical laboratories that will analyze samples collected for WACAP for SOCs, mercury, metals, and major ions/nutrients. Analyses for each indicator (snow, fish, etc.) by analyte (SOCs, mercury, etc.) will be conducted by the same laboratory, but there are some cases where an analyte is analyzed at different laboratories depending on the indicator. For example, mercury in snow will be analyzed by the USGS Wisconsin Laboratory, while mercury in fish, sediment, water, and lichens will be analyzed by the Willamette Research Station (WRS) Analytical Laboratory. The Simonich Environmental Chemistry Laboratory (SECL) will analyze all samples for SOCs, and the USGS Boulder laboratory will analyze all samples for metals.

Address and contact information for each laboratory is listed in Table 3.2.2.

Table 3.1.2 Summary of sampling and analysis plan

Matrix	**SNOW**				
Purpose	Measure of direct atmospheric contaminant loading, and in many cases, 90% of the annual precipitation, interannual variability				
Frequency	Annually; 14 sites in 8 Parks, and additional snow-only sites for elevational transect				
Samples	**Inorganic** Integrated vertical snowpack profile Single Teflon Bag, 6 liters of snow = 2 liters of water To USGS Denver				**Organic** Integrated vertical snowpack profile 6 Teflon Bags, 20 liters of snow each = 42 liters of water To EPA Corvallis
Sample Processing	Filtration thru 0.45µm	Unfiltered, acidified	Unfiltered	Filtration thru GF/F (0.7µm)	Sorbant extractions
Analytes	Filtered, acidified: Ca, Mg, Na, K (IC) Filtered: NO_3, SO_4, Cl, NH_4 (IC) DOC (IR) Unfiltered: specific conductance, pH, ANC	Metals: Cd, Cu, Pb, Ni, V, Zn, plus additional metals listed in Table 2.2.1 (ICP-MS)	Hg (oxidation, purge and trap; CVAFS)	Total particulate C and N (EPA Method 440.0)	Target SOC analytes (GC/MS)
Laboratory	USGS Colorado District Lab	USGS Boulder Lab	USGS Wisconsin Mercury Lab	Chesapeake Bay Lab	SEC Lab

Table 3.1.2 Summary of sampling and analysis plan (continued)

Matrix	**FISH**					
Purpose	Direct measure of food web impacts, bioaccumulation and link to the terrestrial component; evaluation of health and condition effects					
Frequency	Once per site: 4 to 6 sites (2 to 3 parks) per year; PJ Lake in OLYM sampled annually					
Samples	~30 fish/lake (3 fish from each of 5 age classes, from both sexes, from a single species)					
	Condition factors	Hematology/ Physiology	Histopathology (gills, kidney, liver, spleen, gonads)	Whole fish tissue		Livers and fillets (from up to 10 additional fish collected for metals analysis)
Sample Processing		Blood obtained by caudal vein puncture, plasma collected and frozen in the field	Organs preserved in 10% neutral buffered formalin	Homogenization, microwave digestion; extraction with ASE for SOC analyses		Homogenization, freeze drying, microwave digestion
Analytes	Weight, fork length, Macroscopic health index; ages from scales and otoliths	Hematocrits, plasma, cortisol, glucose, sex hormones, and vitellogenin	Evaluation of pathological changes, macrophage aggregate analysis; and reproductive state	Hg (Direct Hg Analyzer)	Target SOC analyses (GC/MS)	Metals: Cd, Cu, Pb, Ni, V, Zn (ICP/MS)
Laboratory	On-site, and OSU Kent Lab	On-site, and OSU Kent and OSU Schreck Labs	EPA Gulf Breeze Lab	WRS Analytical Lab	SEC Lab	USGS Boulder Lab

Table 3.1.2 Summary of sampling and analysis plan (continued)

Matrix	LICHEN			WILLOW BARK/LICHEN/ CONIFER NEEDLES	SUBSISTENCE NATIVE FOOD		
Purpose	Direct measure of food web impacts and bioaccumulation; used primarily to evaluate N, S, and heavy metal impacts			Measure of ecosystem exposure, large "n" for statistical comparisons within and among sites, parks, and elevations	Direct measure of food sources (moose) used by native people		
Frequency	Once per site: collected in 2003 and 2004			Once per site: collected from 8 WACAP Parks in 2004, and up to 12 additional Parks in 2005	Once: Alaska only, ~20 samples		
Samples	6 lichen samples collected per site (3 samples each of 2 species); ~20 g dry weight of material for each sample			Five ~30-cm pieces collected from 3 willow trees at each site (i.e., 15, 30-cm pieces/site), with 5 sites at different elevations per Park	Samples provided to Parks by native hunters		
Sample Processing	Ground thru 20 mesh, then oven dried at 65°C to constant weight			Extraction using ASE	Homogenization, microwave digestion; extraction with ASE for SOC analyses		
Analytes	N, S	Metals: Cd, Cu, Pb, Ni, V, Zn (ICP-MS)	Hg (Direct Hg Analyzer)	Target SOC analytes (GC/MS)	Hg (Direct Hg Analyzer)	Target SOC analytes (GC/MS)	Metals: Cd, Cu, Pb, Ni, V, Zn (ICP-MS)
Laboratory	UMNRAL	USGS Boulder Lab	WRS Analytical Lab	SEC Lab	WRS Analytical Lab	SEC Lab	USGS Boulder Lab

Table 3.1.2 Summary of sampling and analysis plan (continued)

Matrix	WATER		LAKE SEDIMENT				
Purpose	System characterization; standard water quality information	Hydrophilic current-use chemicals and SOCs	Historic trends (~150 years) of contaminant loading to catchments				
Frequency	Once per site: 4 to 6 sites (2 to 3 parks) per year	Once per site: 4 to 6 sites (2 to 3 parks) per year	Once per site: 4 to 6 sites (2 to 3 parks) per year				
Samples	**Inorganic** 2 L water sample, 2 60-ml syringe samples	**Organic** ~50 L water sample filtered *in situ*	Sediment cores, sectioned in 0.5 cm intervals to 10 cm, then 1.0 cm intervals to 30 cm.				
Analytes	*In situ:* specific conductance, DO, temperature, turbidity Filtered: Ca, Mg, Na, K, Zn, Se (AAS), NO3, SO4, Cl, (IC) SiO2, NH4 (AA), DOC (IR), color Unfiltered: TN, TP (FIA), ANC, TSS Syringe "closed system" samples: pH, DIC	Target SOC analytes, particulate and dissolved phases (GC/MS)	Dating profiles (^{210}Pb, ^{137}Cs, ^{241}Am)	Spherical carbonaceous particle analysis	%moisture, Ash-free dry weight (loss-on-ignition) or total organic carbon Hg (Direct Hg Analyzer)	Target SOC analytes (GC/MS)	Metals: Cd, Cu, Pb, Ni, V, Zn (ICP-MS)
Laboratory	WRS Analytical Lab	SEC Lab	Appleby Laboratory-UK	Neil Rose Laboratory-UK	WRS Analytical Lab	SEC Lab	USGS Boulder Lab

Table 3.1.2 Summary of sampling and analysis plan (continued)

Abbreviations:

AAS	Atomic absorption spectrophotometry
ASE	Accelerated solvent extraction
CVAFS	Cold vapor atomic fluorescence spectrometry
FIA	Flow injection analysis
GC/MS	Gas chromatography with mass spectrometry
IC	Ion chromatography
ICP-AES	Inductively coupled plasma with atomic emission spectrometry
ICP-MS	Inductively coupled plasma with mass spectrometry
IR	Infrared detection

Laboratories:

USGS Colorado District Laboratory, WEBB Project, Denver Federal Center, Lakewood, CO
USGS National Research Program (NRP) Laboratory, Boulder, CO
USGS Wisconsin Mercury Laboratory, Middleton, WI
Chesapeake Bay Lab, Solomons, MD
SEC Lab (Simonich Environmental Chemistry Laboratory), Dept. of Environmental and Molecular Toxicology and Dept. of Chemistry, Oregon State University, Corvallis, OR
OSU Kent Laboratory: Dept. of Microbiology, Oregon State University, Corvallis, OR
EPA Gulf Breeze Laboratory: U.S. EPA, Gulf Breeze, FL
WRS Analytical Laboratory: U.S. EPA, Willamette Research Station (WRS) Analytical Laboratory, Corvallis, OR
UMNRAL: University of Minnesota Research Analytical Laboratory, St. Paul, MN
Appleby Laboratory: Dept. of Mathematical Sciences, University of Liverpool, Liverpool, UK
Neil Rose Laboratory: Environmental Change Research Centre, University College London, London, UK

Table 3.2.1 WACAP Laboratories by Analyte Group and Ecosystem Indicator

Ecosystem Indicator	SOCs	Mercury	Metals	Major ions/ nutrients
Snow	SEC Lab*	USGS Wisconsin Lab	USGS Boulder Lab	USGS Colorado District Lab & USGS Boulder Lab
Fish	SEC Lab	WRS	USGS Boulder Lab	
Water	SEC Lab	--	--	WRS
Sediment	SEC Lab	WRS	USGS Boulder Lab	--
Vegetation	SEC Lab	WRS	USGS Boulder Lab	UMNRAL
Moose	SEC Lab	WRS	USGS Boulder Lab	

*SEC Lab: Simonich Environmental Chemistry Laboratory, Oregon State University, Department of Environmental and Molecular Toxicology, Corvallis, OR
USGS: United States Geological Survey,
WRS: Willamette Research Station Analytical Laboratory, U.S. EPA, Corvallis, OR
UMNRAL: University of Minnesota Research Analytical Laboratory, Department of Soil, Water, and Climate, St. Paul, MN

3.3 Collection of Field Duplicates

Each ecosystem indicator has a unique set of circumstances that will affect the number of field duplicates that are collected. Collection of field duplicates for snow sampling will be difficult because the volume and weight of snow required, and the time required to collect snow at some of the remotes sites, will make it very difficult to collect a second sample. Snow is also the only ecosystem indicator that will be sampled every year for three years. An estimate of within-year variability from field duplicates at each site would be helpful when comparing data from year-to-year, but the effort and analysis cost involved in collecting field duplicates at each site is prohibitive. See Table 4.1 for a list of the proposed field duplicates for snow samples.

Collection of field duplicates for other ecosystem indicators will follow a similar pattern, except for sediment. Duplicate sediment cores will be collected, but not analyzed unless there are problems with the stratigraphy in the primary core. Sediment sections from the primary core will be dated using Pb-210 and Cs-137 before any other analyses. The dating profile will determine if the layers of sediment in the core were deposited in chronological order, and if so,

Table 3.2.2 WACAP Laboratory Contact Information

Laboratory	Address	Contact Information
Simonich Environmental Chemistry (SEC) Laboratory	1161 Agricultural and Life Sciences Dept. of Environmental and Molecular Toxicology Oregon State University Corvallis, OR 97331	Dr. Staci Simonich 541-737-9194 staci.simonich@orst.edu Dr. Kim Hageman 541-737-9208 kim.hageman@orst.edu
WRS Analytical Laboratory	Willamette Research Station Analytical Laboratory, U.S. EPA 1350 SE Goodnight Ave. Corvallis, OR 97333	Scott Echols 541-754-4877 echols.scott@epa.gov
USGS Boulder Laboratory	Trace Element Environmental Analytical Chemistry Project U.S Geological Survey National Research Program 3215 Marine St., Suite E-127 Boulder, CO 80303	Howard Taylor 303-541-3007 hetaylor@usgs.gov
OSU Kent Laboratory	Dept. of Microbiology 220 Nash Hall Oregon State University Corvallis, OR 97331	Mike Kent 541-737-8652 or –5088 Michael.kent@orst.edu
OSU Schreck Laboratory	Oregon Cooperative Fish and Wildlife Research Unit 170 Nash Hall Oregon State University Corvallis, OR 97331	Carl Schreck 541-737-1961 carl.schreck@orst.edu
EPA Gulf Breeze Laboratory	U.S. Environmental Protection Agency Gulf Ecology Division 1 Sabine Island Drive Gulf Breeze, FL 32561	Jack Fournie 850-934-9272 fournie.john@epa.gov
USGS Wisconsin Laboratory	Wisconsin District Mercury Research Lab USGS Water Resources Division 8505 Research Way Middleton, WI 53562	David Krabbenhoft 608-821-3843, 608-828-9901 dpkrabbe@usgs.gov
USGS Colorado District Laboratory	USGS – WRD, Colorado District Denver Federal Center, MS-415, Bldg. 53 Lakewood, CO 80225	303-236-4882
UMNRAL	Research Analytical Laboratory University of Minnesota Rm. 135 Crops Research Bldg. 1902 Dudlley Ave. St Paul, MN 55108-6089	ral@soils.umn.edu 612- 625-3101

the core will be considered good and other analyses will proceed. Duplicate cores are not necessary because each core will have approximately 20 sections, and we will be looking for changes in concentration through the chronology represented by the sections.

3.4 Field Blanks

Collection of field blanks for SOC analyses is critical for determination of contamination, yet very difficult to do with remote field sites and with samples that are being extracted with large volumes of organic-free DI water. Ideally, pesticide -free DI water would be brought to each field site and treated the same as a sample. However, that would require 50 to 60 L of water be transported to the field site, then transported back, and shipped to the laboratory. We are planning on using alternatives, especially for snow sampling. Field blank samples will be collected during snow sampling by pouring 4 L of pesticide-free DI water over the shovels used to collect snow samples. This rinse water will be collected in a single Teflon bag, which will be handled and processed like a snow sample. The blank samples may be collected at a nearby location, e.g. at the trailhead where logistical or safety considerations make transport of blank water to the snow sample collection site impractical.

Another alternative would be to bring extra sample containers or extraction columns to the field to be handled in the same manner as if a sample were added. The container would be exposed to ambient air, then transported back to the laboratory along with the regular samples.

4.0 Snow

4.1 Introduction

Snow water equivalent and snowpack concentrations of various contaminants will provide an index of current levels of deposition of those contaminants, and will provide a snapshot of spatial variability in winter deposition to cold ecosystems in national parks of the western United States. Snowpack sampling will be the primary way in which spatial variability of contaminant deposition will be evaluated and quantified. Winter deposition of mercury and organic contaminants may be greater in high elevation and high latitude snowpacks than in those at lower elevations and latitudes. Patterns of contaminant deposition will be used to infer processes of atmospheric transport, atmospheric deposition, transformations in the snowpack, and loading to the ecosystem. Contaminant deposition in the snowpack should be related to contaminant levels in air, lake water, lake sediments, and biotic matrices, thereby linking ecosystem impacts to airborne contaminant pathways and the history of contaminant loading to the catchment.

The seasonal snowpack will be sampled at the time of maximum accumulation during the spring. The time period for snow sampling will be from early March to late April, depending on the conditions each year. Snow will be sampled every spring at the catchment sites in the Parks. If rain-on-snow events have occurred, or snowmelt has begun at the catchment sites by late winter, snow may be sampled at nearby higher elevation sites. In addition, in some parks, an elevational transect, consisting of up to 5 samples collected from a range of elevations, may be collected.

Additional sites for snow sampling will be selected in Mt. Rainier and North Cascades National Parks beginning in 2004. These sites will be selected to provide additional information on elevational gradients, and spatial and temporal variability. A bulk precipitation collector has been installed on Hurricane Ridge in Olympic National Park, and samples will be collected at intervals of 2 to 3 weeks to provide temporally-resolved deposition data. Rain on snow events are a problem in Olympic, and this type of collector will allow complete deposition data to be collected.

Snow samples will be collected by USGS with assistance from the NPS and other WACAP partners. Access to the sites will be by helicopter, snowmobile, skiing, snowshoeing, or a combination of these techniques. Two samples will be collected from each snowpit: one inorganic sample for analysis of major ions, nutrients, dissolved organic carbon, trace metals, mercury, and particulate matter; and one organic sample for analysis of organic contaminants (Figure 4.1).

4.2 Sample Collection

Timing of Sample Collection

Sampling is done near the time of annual maximum snow accumulation but before the onset of spring snowmelt. Timing of maximum accumulation at the sampling site is determined by averaging maximum snow-water equivalence (SWE) values over 30 years from nearby

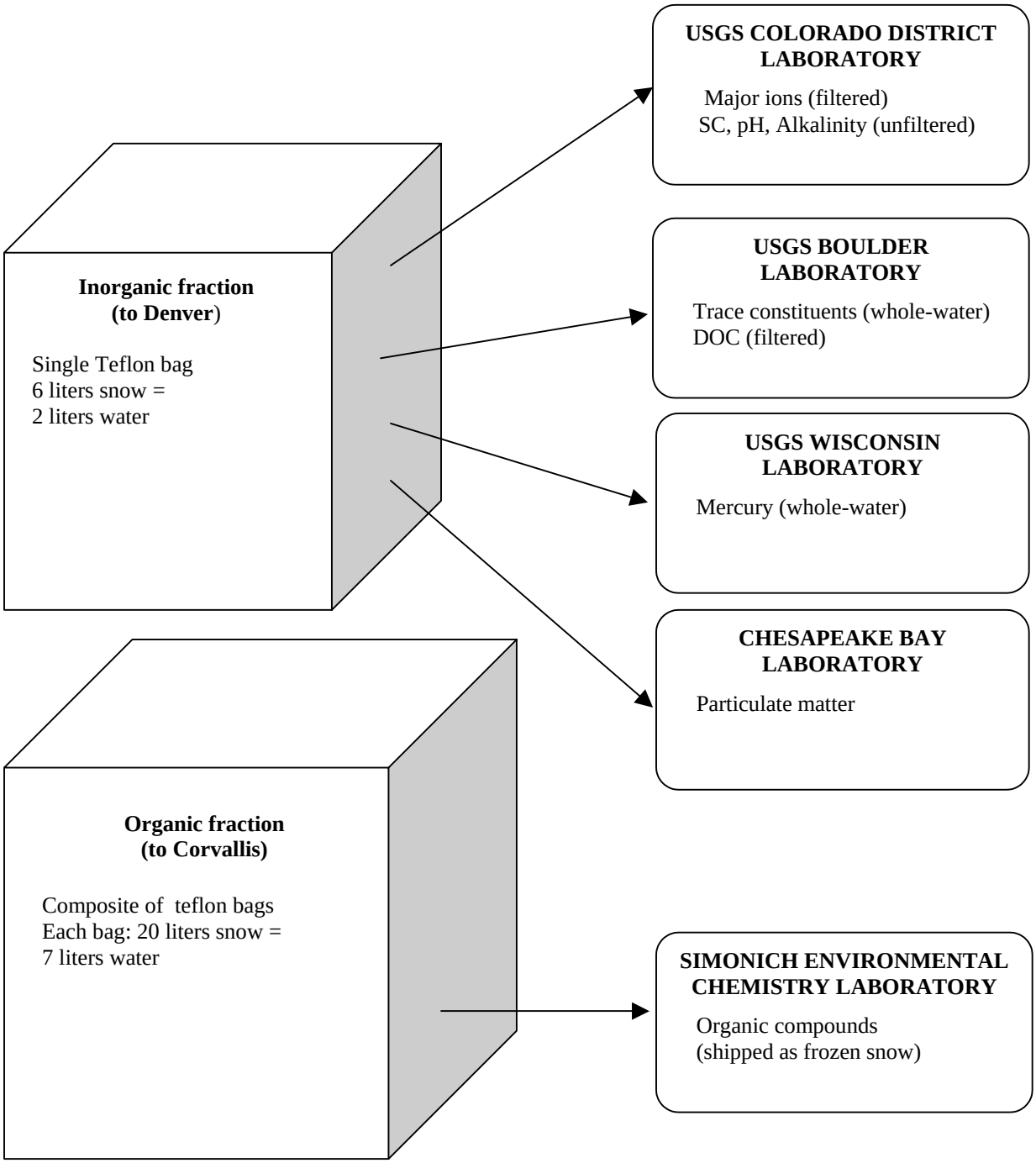


Figure 4.1 Snow sample flow diagram

SnoTel sites at similar elevations. Sampling dates are scheduled 2 or 3 weeks before the average maximum date in order to ensure that samples are collected prior to episodes of early snowmelt. Waiting to capture additional snowfall from a few end-of-season storms is not worth risking loss of part of the seasonal pack to snowmelt. Obtaining snow samples before melt begins is crucial to preserving the chemical record of the snowpack because the liquid water flowing downward through the snowpack in early stages of snowmelt tends to be more concentrated compared to snowmelt occurring later in the process.

Sample Vessel Preparation

Samples for inorganic analyses will be collected in an 8 liter Teflon bag that will contain approximately 6 liters of snow, yielding about 2 liters of meltwater. Sample bags will be prerinsed three times with de-ionized water, placed in polyethylene bags, and frozen until use.

Samples for organic analyses will consist of enough 24"x24" Teflon bags to contain approximately 60 liters of snow, yielding about 20 liters of water. The bags will be pre-cleaned at the SEC Laboratory by rinsing the inner lining once with approximately 45 mL of ethyl acetate, followed by approximately 45 mL or hexane:acetone 1:1. The Teflon bag is allowed to dry, then it is folded and covered with aluminum foil and folded into a 6 inch square. The folded bags are placed into two Ziploc bags and sealed.

Snow Sample Site Selection

Because no construction of permanent structures is necessary for sampling seasonal snowpacks, locations may be selected in the most optimal locations without permanently affecting wild areas in National Parks. The only disturbance at sampling sites is the digging of a small snowpit, which is backfilled just after sample collection. Wind and snowfall events restore smooth, untracked snowscapes soon after sampling visits. Sampling locations are selected that are free from avalanche activity and reasonably accessible to sampling crews.

Samples are collected in small clearings or open areas on cooler, north-facing slopes. Snow cover should be uniform and free of human effects or other disturbances such as excessive tree litter or animal activity. Each layer sampled is inspected for visible contaminants. Scoured or drifted snowscapes are avoided because such areas may not be representative of the cumulative seasonal snowpack from all snowfall events. Sites are located at least 100 m away from plowed roadways to minimize contamination from vehicular traffic.

When possible, snow-sampling sites are located near snow-telemetry (SnoTel) instrument sites operated by Natural Resources Conservation Service for daily measurement of snow-water equivalence (SWE) throughout the western United States. SnoTel sites also report other meteorological information useful in choosing sampling locations for the study, including depths, total annual snowfall accumulations, air temperature, and total precipitation (Western Regional Climate Center, 2001).

Collection of Field Duplicates and Field Blanks

A schedule for collection of field duplicates and field blanks has been developed for the 19 snow sample sites. Each year at least 2 field blanks and 2 field duplicates will be collected for both the SOC samples and the major ions and trace metals samples. Ideally at least one field duplicate would be collected from each Park, but because of access issues, some compromises had to be made. Most of the duplicates and blanks for the Alaska sites will be collected in Denali National Park. However, sampling will be completed by the same person at all Alaska sites each year, and will be done on the same trip. Snow sample collection at Glacier National Park is also very difficult, so extra duplicates and blanks will be collected at Rocky Mountain National Park. See Table 4.1 for a list of the proposed field duplicates for snow samples.

Sample Collection Procedure

At some sites 2 or more samples will be taken in a variety of containers including 15-gal. carboys, or 5-gal buckets, and 2 different-sized Teflon bags (3-kilo, 14"x 22"; and 7-kilo, 24"x 24"). The kinds of samples taken at different sites will vary (e.g. we'll only get samples for isotopes and semi-volatile organic contaminants (SOCs) at selected sites), so double-check your list before heading out to make sure you have the right type and number of containers. After returning to your vehicle with the sample(s), all Teflon-bag samples need to be refrigerated immediately and for the duration of the trip.

1) Locate site

Be careful of avalanche danger along the route--especially in Colorado! If conditions are too hazardous, do not go to the site! Avoid even small-fetch slopes and gullies where avalanches are not typically expected but can snuff a skier. If current storm conditions indicate dangerous loading, choose an optional site in the vicinity along a safer route. With provided site-maps locate as close as possible to sites without placing the party at risk, and take care not to ski or snowmobile over snow-courses or snow-pillows at SnoTel sites. Choose the spot for the sample-pit at least 10m away from snow-courses and SnoTel sites. DOCUMENT LOCATION using hand-held GPS unit or best available landmark descriptions and positions. Report location in degrees, minutes, seconds (NAD83); report horizontal accuracy; and report elevation from 7.5' topographic map or mapping software.

2) Verify sub-freezing snow, dig pit

If there is any doubt that the snow is sub-freezing (below 0 degrees C), dig a narrow, hasty pit about 1 meter down and quickly place a few thermometers at intervals to represent a gradient of most of the top meter of the pack. A temperature gradient, or series of values below zero, is what you want to see. A series of 0.0-temps probably means the pack is becoming isothermal, and another location for the pit needs to be chosen. This quick temperature check can save unnecessary digging and increase odds we'll get a good sample. Look for northerly aspects and moderate slopes with tall trees shading the sun whenever possible.

Once a spot is selected for digging the pit, scribe a line perpendicular to the direction of the sun to delineate the face of the pit wall, dig the pit so the wall faces away from the sun, and avoid walking on or shoveling snow on the snow surface for at least 2 m on the other side of the line (where the pit wall will be sampled). Metal shovels can be used to dig pit. Once pit is prepared, bisect pit wall to be sampled with a 2m fiberglass rule vertically with 0 cm at the soil-

Table 4.1 Field Replicates and Field Blanks for Snow Sampling

PARK	SITE NAME	2003 Majors*		2003 SOCs		2004 Majors		2004 SOCs		2005 Majors		2005 SOCs		
		FLD BLK	FLD REP	FLD BLK	FLD REP	FLD BLK	FLD REP	FLD BLK	FLD REP	FLD BLK	FLD REP	FLD BLK	FLD REP	
NOAT	Burial Lake									1		1		
NOAT	Matcharak													
DENA	Kahiltna Base Camp													
DENA	McLeod Lake													
DENA	Wonder Lake	1		1			1		1		1		1	
OLYM	Hurricane Ridge					1	1	1	1					
OLYM	Waterhole													
OLYM	Hoh Lake													
MORA	Alta Vista	1		1										
MORA	Mowich Lake										1		1	
MORA	Camp Muir													
GLAC	Oldman Lake													
GLAC	Snyder Lake													
ROMO	Lake Irene		1	1	1									
ROMO	Lake Irene Meadow		1		1	1	1	1	1	1	1	1	1	
ROMO	Lone Pine													
ROMO	Mills Lake													
SEKI	Emerald Lake				1	1	1	1						
SEKI	Pear Lake													
	SUMS:													**TOTALS:**
Majors blanks	1 ea. 3kg teflon	**2**				**3**				**2**				**7**
Majors reps	1 ea. 3kg teflon		**2**				**4**				**3**			**9**
SOCs blanks	1 ea. 7kg teflon (1 gal. Organic-free water)			**3**				**3**				**2**		**8**
SOCs reps	6 ea. 7kg teflon				**3**				**3**				**3**	**9**

*Majors = samples collected in 1 3-kg Teflon bag for major ions and trace metals analysis; SOCs = samples collected in 6 7-kg Teflon bags for analysis for semi-volatile organic compounds

snow interface; do sampling on one side, and temperature and stratigraphy work on the other side to avoid contamination of sample-face. The final vertical surface (approx. 50cm wide) of the pit-wall to be sampled should be cut back into the wall with the clean, snow-scrubbed Lexan shovel for an additional 10-20cm at least. This removes any paint, metals, soils, or dirty snow spread around while digging pit. Before samples are collected, clean tools again by plunging polycarbonate scoop and Lexan sampling shovel blade into snow at least 12 times to remove soiled snow and scrub off any remaining snow or water from a previous sample. Do this tool cleaning at an undisturbed corner of the snowpit reserved for tool-scrubbing, and adjacent to the sampling face, while avoiding excavated snow, access steps, equipment, personal gear, skis, and any disturbed snow.

3) Obtain physical measurements, and complete data sheet (Figure 4.2)

A) Fill in location, conditions data, and time (*use same time* for Teflon bag sets and any isotope carboys; use separate times for subsequent replicates and blanks). Please be thorough and keep remarks concise--no extraneous comments.

B) Scale and label snowpack to be sampled by 10cm increments in "Depth" column on datasheet. See example. Clearly mark top of snow pack near *top* of datasheet with exact depth in cm; note snow-soil boundary and clearly mark near *bottom* of datasheet. Make careful notation and physical measurements of:

Thermometer precision: place all thermometers in same layer of snow and note precision before and after measurement of temperature profile. If a single thermometer is out of calibration with the others, set aside and recalibrate in ice-bath before using again. For multi-day sampling, calibration checks in an ice-bath should be done between sites if precision varies by > 0.6 deg. C between thermometers.

Temperatures at 10cm intervals for pits < 2m deep; 20cm intervals for depths >2m.

Individual layers' grain-type (new, graupel, ET, TG, ET/TG, ice lens), grain-size (in mm, use grid card), and hardness. For example, while applying one Newton of force (a moderate push), test if you can push either your fist, 4 fingers, 1 finger, a pencil, or a knife through the pack. Note vertical distance for boundaries of all strata on scribed vertical line of the datasheet (see example datasheet). Note ice lenses, discolored layers, unusual snow, or evidence of rain percolation, etc in remarks adjacent to layer.

Note anything peculiar that might affect chemistry of sample (e.g. vertical ice fingers, animal droppings, urine, etc.). Complete all data including SWE column, and *sign datasheet.*

4) Collect samples

A) SOCs samples (7-kilo, 24” x 24” Teflon bags)

1. Collect SOCs samples after snowpack physical measurements and before the major-ion and isotope samples.
2. Put on 2 or 3 pairs of gloves before handling the sample tools and preparing the final sampling face of the snowpit. Then, if the outer pair becomes contaminated it can easily be removed to expose a clean pair. Put on clean gloves just before taking samples and

Figure 4.2 Snow Sample Field Form

2003 Snowpack Sampling Data-Sheet

Sample type	# of bags	Sample time(s)	Lab ID
Std Rocky Mt. Snowpack, 3-kilo Teflon bag, (note: 5-gl buckets & 15-gl carboys get same time)			
3-kilo Teflon bag, replicate			
3-kilo Teflon bag, field blank,			
WACAP, SOCs, 7-kilo Teflon bags			
USGS/NPS, SOCs, 7-kilo Teflon bags			
7-kilo Teflon bag, replicate, (project: _____)			
7-kilo Teflon bag, field blank, (project: _____)			

Site name:	**Sample Date:**	**Total snow depth (cm):**
Lat: Long:	Elev:	Check isotope samples collected: ____ ^{15}N, ____ ^{34}S
Observers:	Aspect:	Slope:
Air temp (^{o}C):	Weather:	

Thermometer precision: record range of values in same snowpack layer before sampling _____ ^{o}C, and after _____ ^{o}C
Soil condition under snowpack? moist? muddy? frozen? dry?
Pit location description:

Depth interval (cm)	Temp (^{o}C)	Sketch layers by grain type (TG, ET, MF, new)	Grain size (mm)	hardness (K, P, 1F, 4F, or fist)	SWE (g)	comments

More cells on reverse

Signatures of Observers:_____

Figure 4.2 Snow Sample Field Form (continued)

Continue from front page if necessary:

Depth interval (cm)	Temp (^oC)	Sketch layers by grain type (TG, ET, MF, new)	Grain size (mm)	hardness (K, P, 1F, 4F, or fist)	SWE (g)	comments

always between samples if hands need to be re-warmed before all samples are collected. When in doubt, change your gloves. Any organic chemicals are potential sources of contamination for these samples so be aware of things like food & beverages, solvents, sun screen, insecticide, snowmobile exhaust, soil, etc..

3. Clean the polycarbonate scoop and the Lexan shovel blade by plunging into clean, untouched snow at least 12 times to scrub off any potential contaminants. These tools will have been pre-cleaned in the lab with strong soap, then rinsed 3 times with tap water, soaked in DI water, and rinsed 6 times in DI water before being placed in a clean, heavy-duty poly bag for transport to the field. Place the tools back in the clean poly bag for return transport and subsequent sampling.

   Do not touch shovel blade or scoop surfaces other than handles. Clean the pit face with the newly-scrubbed and clean Lexan shovel used for major ion and trace metal sampling. Sampling tools (Lexan shovel and polycarbonate scoop) may be temporarily placed in area where clean snow scrubbing was done to free hands for other tasks, but tools should be kept away from areas where potential contamination may occur and scrubbed again in clean snow if necessary before beginning or resuming sampling.

4. Before sampling, remove outer gloves and clean the face once more with clean Lexan shovel and the polycarbonate scoop.

5. Collect the SOCs sample in the same manner as the major ion/trace metal sample outline in section (B) below. The only difference is that SOCs bags are larger. The Teflon bags will be pre-cleaned in the lab with organic solvents, then sealed with aluminum foil and double bagged in Ziplocs. After opening each bag, discard aluminum foil. While sampling, do not touch the inside of the Teflon bag with anything except the sample tools. Take extra care to not allow contaminants from clothing, sweat, etc, to get into the sample when filling with snow or gathering the opening to close the bag. Do not force the bag to maximum capacity; stuffing excessive masses of snow into the bags will stress the seams. Only a moderate amount of compaction is necessary, and ~80% volume will likely yield the desired 7 liters of melt water per bag. A per-bag mass can be determined by suspending the sample bag by the provided fish scale with an extra cable tie placed around the bag after it has been sealed to ensure enough snow is being collected.

6. Six each 7-kilo Teflon bags will be collected for each WACAP snow sample. Two 7-kilo bags will be collected for each USGS/NPS Partnership project snow sample (Glacier and Rocky Mt. NPs only). All sets of samples should be labeled sequentially as 1 of 6, 2 of 6,…6 of 6. In order to obtain a more representative sample, be sure to collect a sample of the entire snow column in each bag. To do this efficiently, and to avoid overfilling the bag before depth-integration is complete, do several top-to-bottom depth-integrations of the whole pack (except for the bottom- and top 5-10 cm) for each of the bags per site.

7. After sampling is complete, close the bag using 2 cable ties, place the Teflon bag inside a black plastic bag, and place that package along with the sample label inside a clean, heavy-duty poly bag. Vapors from marking-pen ink could be a source of organics or metals so make sure your sample label is inside it's Ziploc bag before you put it in the

outer poly bag. Ensure label is visible, wrap poly bag, and securely duct-tape it for transport.

8. Cover samples with snow to keep them cold until you are ready to leave the field site. Take precautions to avoid sunshine from heating the samples because of the heat-absorbing black plastic bags involved. Place inside coolers and preserve with dry ice or blue ice ASAP.

9. For SOCs field blanks, distinguish between either the USGS/NPS Partnership project or the WACAP project. At USGS/NPS Partnership sites, pour a minimum of 5 but not more than 6 liters in each of two bags (total 10-12 liters) of pesticide-grade DI over the Lexan shovel and polycarbonate scoop into a clean Teflon bags. At WACAP sites 4 liters of the same pesticide-grade blank water will be washed over the same sample tools into 1 Teflon bag. Leave some airspace when you close the blank bags to accommodate for expansion when the water freezes.

B) Major-ions and trace-metals samples (3-kilo, 14” x 22” Teflon bag):

Avoid contamination of very dilute snow samples from soil, forest litter, sweat, nose-drippings, etc. Do not touch the inside of the Teflon bag. With all workers doing sampling wearing latex gloves provided, one person holds Teflon bag open being careful not to touch inside of bag, and not to tear it at the seam, while another person scoops out a vertically representative column of snow using the Lexan snow shovel and the polycarbonate scoop provided. This process can be tedious in a deep and/or very consolidated snowpack. One method that works well is to cut into the face with the polycarbonate scoop about 1-2cm (for a 2m snowpack for example, more or less as depth varies) and remove a column of these dimensions by 10-15cm increments starting at the top and working downward. Discard the top 2cm of snowpack at snow-air interface. With snow-shovel cutting horizontally into column to be removed, vertically scoop out sample down to shovel with polycarbonate scoop provided, and dump this increment into the bag. Repeat at 10-15cm intervals downward until within about 5cm of soil. Stop there, and repeat (if necessary to fill bag 2/3 full) with thin columns by scraping lightly up the face collecting roughly equal amounts of sample from all layers. If soil gets on blade or scoop, plunge into snow away from sample-face 12 times to clean. Fill to no more than 2/3 full to allow for closure of the bag. Shape bag in roughly rectangular shape that would occupy 1/2 of the space in a 12" x 12" x 12" box before the snow sets up--basketball shaped samples do not store efficiently. No need to overfill sample-bag.

To seal the 3-kilo bag, gather open end of bag allowing air to escape, then twist end to form a stub to put plastic tie around. Tightly close 2 cable ties as a precaution in case one tie fails. Be careful not to tear Teflon. Do not write on Teflon bag. Place sample inside of heavy duty poly bag; display label (in it's own sandwich-sized bag) with sitename, date, and time visibly; and wrap and duct-tape heavy-duty bag securely for transport to vehicles. In your vehicle, secure samples in ice chests with blue ice or dry ice--do not use snow that may melt and contaminate sample.

C) Field blanks at standard Rocky Mt. Snowpack sites:

For indicated sites, a field blank will be taken directly after the snow-samples have been collected. Rinse shovel and scoop used for the snow sample with 2 liters of QA/QC deionized water (provided in Teflon bottle, and drawn from isolated Colorado District ultra-pure deionized water) into separate Teflon bag. Pour about 1 liter each over the shovel blade and scoop rinsing most of the surface used to cut the snow samples. Seal Teflon bag with cable ties securely, but allow for expansion of ice when blank is later frozen.

D) Sulfur- and nitrogen-isotope samples:

With same Lexan shovel, remove another representative vertical column of snow filling the 15-gal. carboys or 5-gal. buckets. Avoid sampling the bottom 5cm of snow on the soil. Use clean plastic tools to remove any visible forest litter, pine needles, sunglasses etc. Seal lid of carboys and buckets with 3 to 5 circumferential wraps of duct tape (as when sealed empty) to ensure a tight, strong seal. Samples then can be transported out on a tow-behind skier's sled on it's side, or on a snowmobile without risk of popping open; a tight seal also keeps out gases from vehicles in transit. Label duct tape with sitename, date, time (same time as Teflon-bag sample), and type of isotope, either **S34** or **N15**. Store Lexan shovel blade and ice scoop in poly bag to keep clean for next site.

E) Document any deviations from protocol or problems encountered.

4.3 Sample Transport and Storage

1) Freeze Teflon-bag samples

Maintain temperature below -5 degrees C until delivery of samples and blanks to the walk-in freezer in the USGS facility in building 25. Add dry ice to refreeze blue ice as needed. Be aware of potential CO2 gas poisoning when opening the truck up after long periods of being securely closed up--as in mornings, or for long periods on the highway. Symptoms are odd taste in mouth and drowsiness; a little periodic ventilation will prevent this from becoming a problem. Two 3-kilo samples will fit into each 12"x12"x12" cardboard box (for walkin-freezer storage); label outer side of box with the 2 samples' sitenames for inventory and retrieval purposes and seal with duct tape or tuck box-lids.

2) Transport Teflon-bag samples in coolers; 5-gal buckets and 15-gal. carboys upright

Upon reaching vehicles, position buckets and carboys upright for subsequent melting. Deliver to personnel listed below in Bldg 53, Denver Fed. Ctr. For shipment of Teflon bag samples, use protective coolers, adequate insulation, and blue- or dry ice. DO NOT SHIP SNOW SAMPLES TO ARRIVE ON A WEEKEND DAY--ENSURE SAMPLE(S) WILL ARRIVE FROZEN MON-FRI. PLEASE NOTIFY PERSONNEL BELOW THAT SAMPLES ARE

ENROUTE SO THEY CAN BE RECEIVED AND TRANSFERRED FROZEN TO WALK-IN FREEZERS.

Please notify USGS of shipping arrangements, contact George Ingersoll (303)236-4882 x292 for advance notice NLT the day samples will ship.

IMPORTANT:
Samples will be shipped to 2 different locations depending on the project:

1) Rocky Mountain Snowpack and USGS/NPS partnership samples ship to USGS in Denver:

USGS/WRD
Mail Stop 415
Federal Center
Denver, CO 80225 Attn: Heather Handran

2) WACAP SOC samples ship to WRS Analytical Laboratory in Corvallis:

Richard Kovar
WRS Analytical Laboratory, c/o USEPA
1350 SE Goodnight Ave.
Corvallis, OR 97333

541-754-4735

kovar.richard@epa.gov

If further contact is necessary, notify Heather Handran x241, Don Campbell (303)236-4882 x298, Dave Clow x294, Alisa Mast x314, Leora Nanus x250, Dave Manthorne x321, or Virgie Lowe x261.

4.4 Sample Preparation and Analysis

Organic analyses of snow samples will be conducted at the Simonich Environmental Chemistry Laboratory at Oregon State University (see Appendix A for the QA Project Plan and Standard Operating Procedures). The goal of the analytical method used to extract snow samples is to quantitatively extract 50 L of melted snow, using sorbant extraction. We will extract the particulate and dissolved phases together for a bulk deposition measurement because we are interested in the total deposition to the ecosystem. A bulk deposition measurement of snow has routinely been used by Canadian researchers (Blais et al., 1998; Donald et al., 1999). Because the target analytes have a wide range of polarities, it is unlikely that a single sorbant resin will extract all of the target analytes quantitatively. There is evidence that C_{18} and XAD-2 resins do not efficiently trap polar analytes, like the organophosphorus pesticides and the triazine herbicides and their degradation products, from water efficiently (Sandstrom et al., 2001).

Based on the PI's previous experience with extraction disks (Simonich et al., 2000; Simonich et al., 2002), we have been investigating the use of a hydrophilicly modified and a

hydrophobicly modified divinylbenzene Speedisk sorbant for the extraction of the target analytes listed in Table 6.1 from water. In the PI's experience, the Speedisk technology is superior to 3M's Empore technology because a graded pre-filter allows for extraction of water samples with moderate to high suspended solids, with improved flow rates. Our initial investigations have found that the combination of these new phases results in quantitative recovery of all of our analytes from 1 L of water and is superior to C_{18} (Empore and Speedisk technologies) and XAD-2 sorbants for our analyte list. Excess water is removed from the extracts with sodium sulfate and, to date, no further extract purification has been needed.

Trace metals analyses will be conducted at the USGS National Research Program Laboratory (see Appendix B for QA Project Plan), and major ion analyses of snow samples will be conducted at the USGS Water, Energy, and Biogeochemical Budgets (WEBB) Colorado District Laboratory (see Appendix C for QA Project Plan).

5.0 Fish

5.1 Introduction

The objective of the fish sampling component of WACAP is to determine if airborne contaminants impact fish health in high mountain lakes and to link contaminants in fish tissue to other ecosystem components. Two major approaches will be used: 1) chemical analysis of tissues and 2) evaluation of pathological and physiological changes in fish. We will assess fish as bioaccumulators of contaminants, and correlate fish health and condition parameters and contaminant concentrations with environmental contaminants in other ecosystem components (snow, sediment, water). Correlations of fish health and condition parameters will be provided for specific pollutants and the specific lakes selected for the study.

Fish were chosen as they are immersed in the aquatic environment, and thus would be in intimate contact with the putative contaminants. Moreover, they are keystone species in lakes of all western National Parks where they occur, and as top aquatic predators are very likely to bioaccumulate contaminants. In addition, these bioaccumulated compounds may also be trophically transferred to birds of prey (e.g., osprey), and potentially humans that forage within the parks. An ancillary contribution of this task will be the description of health and reproductive parameters and indices of fishes of our National Parks; such information is heretofore nonexistent for any species of fish in the wild in mountain lakes.

Our target sample will include several age classes with at least 3 fish from each age class and both sexes from a single species. Approximately 30 fish will be collected per lake to obtain a distribution of ages. We will age fish by either scales or otoliths (ear bones which have rings useful for aging). We will try to sample the same species fish (in most cases salmonids) from an individual lake.

The same fish will be used for both chemistry and pathology/physiology for the following reasons: 1) this strategy will allow us to correlate chemical burdens directly with health changes on individual fish; 2) this strategy will likely reduce the overall number of fish collected at each lake, which is very important at lakes with sparse populations; and 3) examination of the same fish for pathology and chemistry is consistent with the EMERGE program in Europe.

5.2 Laboratory Organization and Responsibilities

Three laboratories participate in the fish sampling, processing, and analysis for WACAP: OSU Kent Laboratory, OSU Schreck Laboratory, and the EPA Gulf Breeze Laboratory (see Table 3.2.2). Following are the personnel in the research team with their primary responsibilities:

Carl Schreck, PhD, Co-Principal Investigator, directs WACAP fish efforts.

Mike Kent, PhD, Co-Principal Investigator, directs WACAP fish efforts.

Jack Fournie, PhD, pathological examination of fish tissues.

Jennifer Ramsay, MS, Graduate Research Assistant (doctoral), fish and tissue collection.

Adam Schwindt, MS, Project Leader, coordinates sampling, assay development and sample analysis, data interpretation, and dissemination of results.

5.3 Summary of Fish Analyses

Table 5.3 summarizes the measurements and analyses that will be conducted on fish samples, the methods used, and the precision objectives. Following are brief descriptions of the analyses that will be used:

1. Condition Factors, including weight, fork length, and macroscopic health: These measurements provide a gross evaluation of external and internal changes for general health and will be recorded based on Adams et al. (1993), including external and internal examination of body surfaces, fins, eyes, gills and buccal cavity for gross abnormalities. Fish are measured and weighed in the field immediately after capture.
2. Aging: Scales and otoliths will be collected for aging.
3. Gonads: Gonads will be examined for sex determination, maturation state, and gross abnormality (e.g. ova-testis).
4. Hematology/Physiology: The following data will be collected from blood samples, obtained by caudal vein puncture:
   a. Hematocrits: Hematocrits are processed on site with a portable centrifuge, and expressed as the percent of packed red blood cells per total blood volume.
   b. Plasma: 1 ml removed from the fish for analysis of:
      i. stress parameters: cortisol, glucose. These parameters are useful as indicators of acute stress, i.e., an indication of the immediate health status of the fish when it is euthanized.
      ii. reproductive parameters (sex steroids): Estradiol, testosterone, 11-ketotestosterone, 17α, 20βdihydroxyprogesterone, and vitellogenin will be quantitatively measured by radioimmunoassay.
5. Histopathology: Samples from the following organs will be collected and preserved from each fish: liver, kidney (posterior and anterior), spleen, gonad, and gill. In addition, any abnormal structure or lesion will be preserved.
6. Stomachs: Stomach contents will be saved for diet analysis, i.e., food selection may influence pathways of bioaccumulation. Contents will be preserved in 70% ethanol in screw-top vials.
7. Chemistry: The remaining carcass and blood will be digested for SOC and Hg analysis. Up to 10 additional fish will be collected for metals analyses, using only the livers and fillets from these additional fish for digestion and metals analysis.

Table 5.3 Fish Analyses, Methods, and Precision Objectives

Parameter	Rationale	Method	Precision Objectives
Fork Length	For calculating condition factor		±0.25 cm
Weight	For calculating condition factor		±1 g
Scales	For aging	Counting rings	±1 year
Otoliths	For aging	Counting annulus (sum of one opaque and hyaline layer)	±1 year
Blood			
Hematocrit	Assessment of blood volume	Microcentrifuge	Subjectively estimated
Cortisol	Stress	Stress parameters– cortisol (RIA, modified from Redding et. al.1984)	7% RSD intra-assay 15% RSD inter-assay
Glucose	Stress (if enough plasma is available)	Nova biomedical blood analyzer	QC sample concentration to match range given for that lot
Plasma for chemistry	Saved for possible future chemical analysis		
Reproduction parameters	Effects on sex and reproduction, evidence of endocrine disrupting compound (EDC) exposure	Measurement of sex hormones: Estradiol, testosterone, 11-ketotestosterone, 17α, and 20βdihydroxyprogesterone will be assayed by RIA, and vitellogenin will be measured by ELISA.	5% RSD intra-assay 10% RSD inter-assay
Macroscopic Health Index	General Health	Gross inspection of external and internal aspects for abnormalities	Subjective, e.g. frayed fin, missing eye
Histopathology	Evaluation of pathological changes	Preserved in formalin, processed for histology. Slides evaluated by trained pathologists	Slides read independently by two pathologists
Histopathology: Macrophage aggregates	Evaluation of increase in numbers and size of MA's reflects exposure to contaminants	Preserved in formalin, processed for histology. Slides evaluated by trained pathologists. Exact method TBD but will likely use SPOT software to calculate melanin coloration with unstained tissue as a blank.	TBD when the methodology is finalized.

5.4 Sample Collection

Fish samples for pathology and physiology must be collected fresh and results correlated with macroscopic observations, other field data, and chemistry results. Various collection methods will be utilized as warranted (see Table 5.4). We will first attempt to catch fish by hook and line at each lake. If this is not successful, then gill nets or set lines will be employed.

We will save pieces of individual organs from fish for pathology/physiology studies, and save the remaining carcass for chemical analysis. Pathology/physiology will require about 10% of the blood, 50% of the kidney, the entire spleen (at least for smaller fish), and about 25% of the liver. For other organs (e.g., gills, skin, muscle, gastrointestinal tract) only 10-20% of these organs are needed. We will calculate the overall % of total weight removed from the fish due to these pathology procedures.

5.5 Field Processing

Fish samples will be processed immediately after capture at lakeside. Fish will be separated based on size following the strategy in Figure 5.5.1. Some fish will be used for chemistry and pathology/physiology, and others for chemistry only. Fish for trace metal analysis will be sampled only for otoliths, then shipped to the USGS Boulder Laboratory for further processing for metals analysis in livers and fillets. This strategy was developed in case fish numbers and distribution (age and sex) are limiting, and are based on the priority of WACAP objectives from SOCs/Hg > pathology/physiology > metals. All fish taken will be in keeping with permit limits. Some judgment calls may need to be employed in the field in the event of non-ideal fish numbers or distribution, and/or unsafe sampling conditions.

After collection, species of fish will be identified, and then they will be euthanized with a sharp blow to the head (see Figure 5.5.2), weighed and measured. Data for each fish will be kept separate; each fish will be assigned a number, which will be used on all lab samples. For histopathology, nalgene bottles externally labeled will house the labeled histology cassettes. After processing, the slides will be labeled the same as the cassette with the replicate slides indicated. Plasma will be stored in 0.5 ml tubes labeled with the fish number and frozen immediately on dry ice.

The protocol for field processing of fish samples is as follows:

1. With gloved hands, blot fish dry on labeled towel. Weigh (g) and measure fork length (cm). Towel stays with fish until fish is packaged. Gloves are changed between days, lakes, and parks; only dissecting instruments are used to touch the inside of fish.
2. Record condition factors of each fish according to the Health Assessment Index in Figure 5.5.3. Use the data sheet in Table 5.5.
3. Physiology/Hematology: Bleed *all* fish before proceeding. Sever caudal peduncle.
    a. Remove 1 ml of blood with heparanized syringe and transfer to 0.4 ml microcentrifuge tube. Transfer to ice bath until there are enough tubes to centrifuge (4 tubes). With hand-driven centrifuge spin blood 5 minutes at maximum speed. Estimate the depth of packed red blood cells by visual examination and express as percent of total blood volume.

Table 5.4 Fish Capture Procedures

Angling – most effective before sun hits water and at dusk

1. Capture fish by angling (fly-fish, bait, lure, set-line). Trolling by float tube is effective. Land fish as soon as possible and gently remove hook. Identify species and release unharmed if not desired species. If cannot identify species, or if fish is desired species, continue to 2.
2. Place fish in live cage until several are obtained for identification and workup.
3. Transport fish to fish work-up station. Euthanize fish as needed by blow to head.

Gill net – to occur overnight for increased effectiveness – 2 or 3 people

1. Locate 1 qt. water bottle, fill half full of water to make float. Locate stuff sack anchor and fill with rocks.
2. Crew member 1 holds small mesh end of net on shore while 2 and/or 3 boats (inflatable raft or float tube) move away perpendicular to shore, releasing the net as they go.
3. When entire length is reached, pull taut, release net with attached anchor and float (to top end of net). Let net sink to bottom.
4. Shore crew secures net to vegetation/rock with parachute cord at immediate water-land interface to reduce incidental terrestrial animal capture.
5. Crew should inspect net for tangles, debris, or other anomaly affecting fish capture.
6. Live fish may still be obtained during overnight set. Save live fish for SOCs and histology. Remaining are SOCs and metals only.
7. During net check, paddle along net and pull-up checking for fish. Bring live cage to fill with lake water to hold fish. Allow to re-sink after checking a portion of the net.
8. To remove fish, one crew-member holds float line, the other *carefully* removes fish (gills are easily damaged). Place fish in live cage with water. Finish removal quickly and euthanize on shore.
9. If desired numbers were not obtained, allow net to remain sunk and check regularly.
10. When finished, follow float line from shore pulling net up so you know where the end is. At the end, gather net by holding end in one hand and retrieving at arm's length each time adding more net to the opposite hand. Carefully remove debris as you go.
11. Rinse net with clean water. Store net in stuff sack in the shade. UV ruins monofilament line.

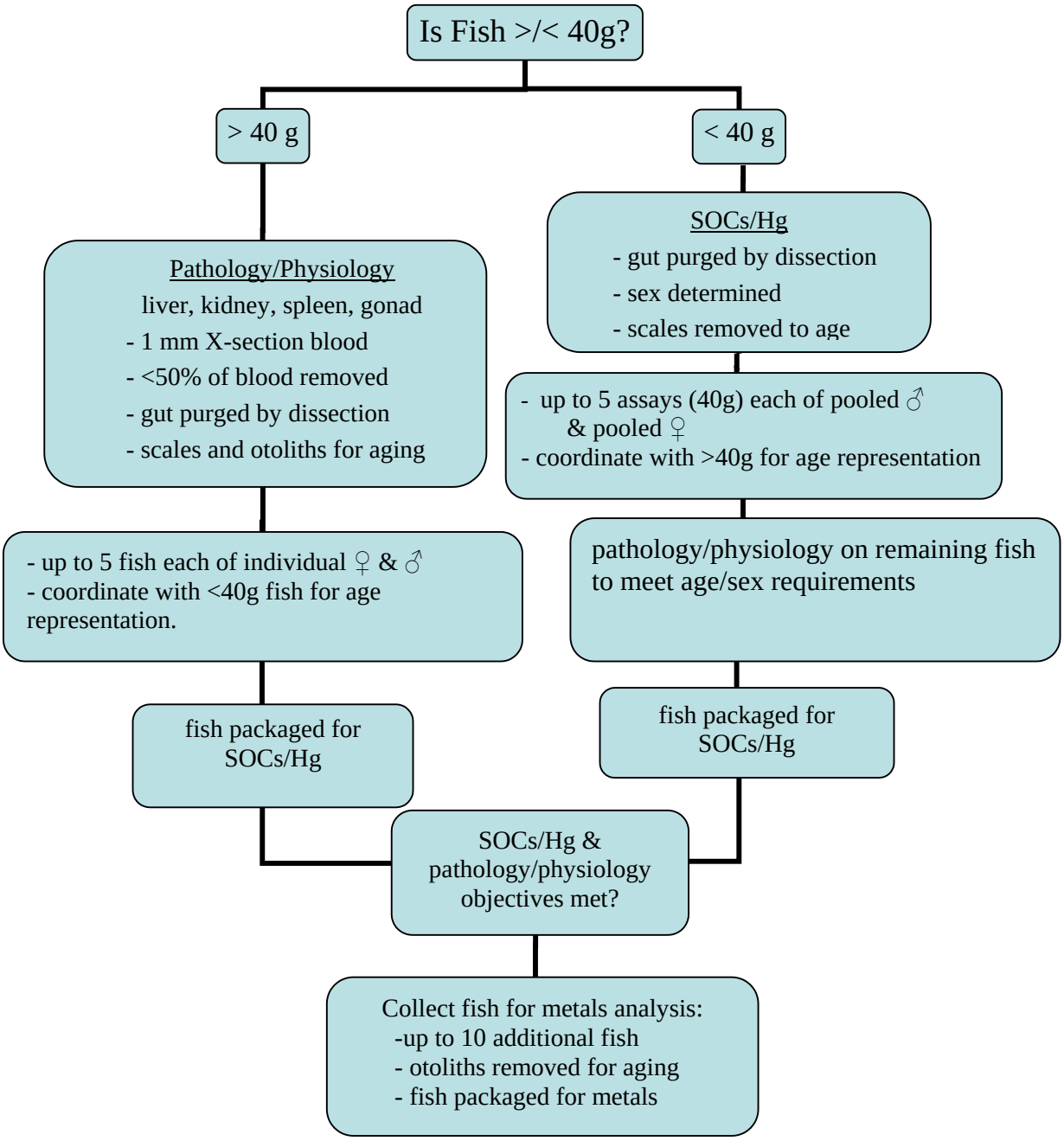


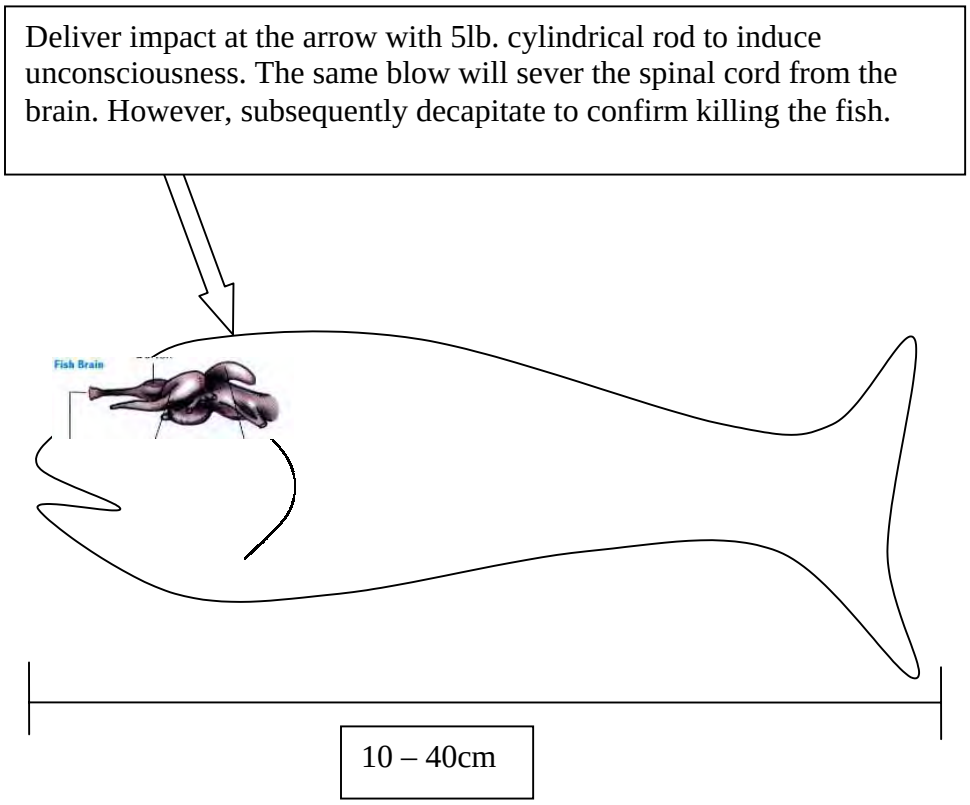
Figure 5.5.1 Fish Processing Strategy

1. Have cylindrical rod for euthanasia ready prior to handling fish.

2. Grasp fish while still suspended in dip net, holding onto both fish and dip net.

3. Grasp rod, raise arm to head level and lower quickly and forcefully. The force should be somewhat less than that required to drive a nail into wood.

4. The figure below demonstrates the location of blow delivery. The caption indicates likely results and subsequent procedures.



Delivering a blow to head followed by decapitation is a humane method of euthanasia for fish (Beaver et al., 2001). This method is preferred, as transporting and using tricaine methanesulfonate in the backcountry of national parks is unacceptable.

Figure 5.5.2 Fish Euthansia Procedure

Variable	Variable condition	Original field designation	Substituted value for the HAI
Thymus	No hemorrhage	0	0
	Mild hemorrhage	1	10
	Moderate hemorrhage	2	20
	Severe hemorrhage	3	30
Fins	No active erosion	0	0
	Light active erosion	1	10
	Moderate active erosion with some hemorrhaging	2	20
	Severe active erosion with hemorrhaging	3	30
Spleen	Normal; black, very dark red, or red	B	0
	Normal; granular, rough appearance of spleen	G	0
	Nodular; containing fistulas or nodules of varying sizes	D	30
	Enlarged; noticeably enlarged	E	30
	Other; gross aberrations not fitting above categories	OT	30
Hindgut	Normal; no inflammation or reddening	0	0
	Slight inflammation or reddening	1	10
	Moderate inflammation or reddening	2	20
	Severe inflammation or reddening	3	30
Kidney	Normal; firm dark red color, lying relatively flat along the length of the vertebral column	N	0
	Swollen; enlarged or swollen wholly or in part	S	30
	Mottled; gray discoloration	M	30
	Granular; granular appearance and texture	G	30
	Urolithiasis or nephrocalcinosis; white or cream-colored mineral material in kidney tubules	U	30
	Other; any aberrations not fitting previous categories	OT	30
Skin	Normal; no aberrations	0	0
	Mild skin aberrations	1	10
	Moderate skin aberrations	2	20
	Severe skin aberrations	3	30
Liver	Normal; solid red or light red color	A	0
	"Fatty" liver; "coffee with cream" color	C	30
	Nodules in the liver; cysts or nodules	D	30
	Focal discoloration; distinct localized color changes	E	30
	General discoloration; color change in whole liver	F	30
	Other; deviation in liver not fitting other categories	OT	30
Eyes	No aberrations; good "clear" eye	N	0
	Generally, an opaque eye (one or both)	B	30
	Swollen, protruding eye (one or both)	E	30
	Hemorrhaging or bleeding in the eye (one or both)	H	30
	Missing one or both eyes	M	30
	Other; any manifestation not fitting the above	OT	30
Gills	Normal; no apparent aberrations	N	0
	Frayed; erosion of tips of gill lamellae resulting in "ragged" gills	F	30
	Clubbed; swelling of the tips of the gill lamellae	C	30
	Marginate; gills with light, discolored margin along tips of the lamellae	M	30
	Pale; very light in color	P	30
	Other; any observation not fitting above	OT	30
Pseudobranchs	Normal; flat, containing no aberrations	N	0
	Swollen; convex in aspect	S	30
	Lithic; mineral deposits, white, somewhat amorphous spots	L	30
	Swollen and lithic	S&L	30
	Inflamed; redness, hemorrhage, or other	I	30
	Other; any condition not covered above	OT	30
Parasites	No observed parasites	0	0
	Few observed parasites	1	10

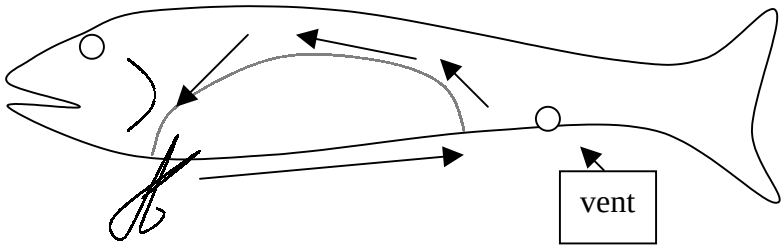
Figure 5.5.3 Health Assessment Index (from Adams et al., 1993)

Table 5.5 Fish Condition Factor Field Form

lake		date		crew			autopsy tech								
fish no.	thymus	fins	spleen	hindgut	kidney	skin	liver	eyes	gills	psdo brch	parasites	Hct	Lct	plsm prot	K
P1															
P2															
P3															
P4															
P5															
P6															
P7															
P8															
P9															
P10															
P11															
P12															
P13															
P14															
P15															
P16															
P17															
P18															
P19															
P20															
P21															
P22															
P23															
P24															
P25															
P26															
P27															
P28															
P29															
P30															

b. Transfer plasma with glass transfer pipette to 0.5 ml plasma tube. Freeze on dry-ice.

4. Gill: Clip 2nd right gill arch (fish snout points to the right). Place in cassette and transfer to 10% formalin.
5. With fish on side, puncture ventral aspect posterior to pectoral fins. Use scissors to cut body-wall posterior stopping 1 cm before vent. Remove body wall with scissors curving up toward spine, then anterior toward head, then ventral ending at initial puncture. Be very careful not to puncture organs. Keep body wall with fish, and include body wall when fish is packaged for shipping.
6. Liver: Care must be taken to avoid gall-bladder puncture. Snip 0.5 cm^3 from anterior aspect, place in cassette and immerse in formalin.



7. Kidney: Expose by removing air-bladder. Remove 1 cm of kidney by first slicing with scalpel and removing with small scupula. The kidney is a diffuse organ, so take care to keep it in one piece. Place between foam in cassette and immerse in formalin.
8. Spleen: The spleen is immersed in the fat ventral to the stomach. Remove with scissors (no fat), place in cassette, and immerse in formalin.
9. Gonad: Determine sex. Gonads reside on either side of the kidney in immature fish, and are long and stringy for male, and slightly thicker orange-ish elongation in female. In mature females you will see eggs. In males the gonads will resemble fat, reside in the same location as the fat, but will be slightly granular in appearance.
10. Stomach contents: Remove stomach and cut open with scissors. Scrape contents into a 5 ml, plastic scintillation vial filled two-thirds full with 70% ethanol.
11. Scale/otolith: Remove scales with scalpel from right side of fish and place on a paper card with the fish number. To remove otoliths, sever spinal column behind head, sever snout just behind nares, remove skull with forceps, and remove brain carefully. Otoliths reside in two very small depressions dorsal and slightly anterior to the eye. Place two in 0.5 ml plastic vials. Five scales or two otoliths per fish will be taken.

5.6 Sample Packaging, Storage, and Shipping

Fish for SOC and Hg analyses will be packaged as follows:

1. Obtain pre-labeled ziploc bag with baked aluminum foil from Simonich Laboratory.

2. With gloved hands cut fish into ~ 5 cm lengths and lightly wrap in baked aluminum foil so that frozen fish won't stick to foil. Be sure that all entrails make it back into fish and foil.
3. Place fish in ziploc bag, add fish id tag, including WACAP number (e.g., 36201) and descriptor number (e.g., MS27), then freeze fish on dry ice.
4. Dry ice must be in contact with fish. Arrange in cooler so that layers of fish are separated by ice. At the end of sampling, if cooler is not full, fill up empty space with paper.

Fish for metals analyses will be packaged as follows:

1. Place fish into new ziploc bag.
2. Add identification tag. Be sure tag contains WACAP number (e.g., 36201) and descriptor number (e.g., MS27).
3. Seal and freeze on dry ice.

Fish, fish tissue, blood, and plasma samples will be stored on dry ice in coolers as soon as possible after collection, and will be transported in coolers. Coolers will be shipped via overnight courier to the OSU Kent Laboratory, where the samples will be stored frozen. Laboratory staff will inventory samples and store at –80°C until further processing.

Organs and organ samples will be fixed in 10% neutral buffered formalin in histological cassettes immediately after dissection. The histological cassettes will be submersed in 1L nalgene bottles, which are packed inside foam coolers. The foam coolers will be placed in cardboard boxes for protection. Absorbent material will be placed inside the case to account for a highly unlikely leakage event. Upon arrival at the OSU Kent Laboratory, the formalin will be replaced with double-distilled H_2O and sent to the EPA Gulf Breeze laboratory for histological sampling. Tissue paraffin blocks and slides will be label with the same number as found on the cassettes.

All samples from a given collection and station will be assigned a pathology code by Schwindt. Frozen fish and tissues for SOC analyses will be hand delivered to the Simonich, OSU Laboratory.

5.7 Sample Preparation and Analysis

SOC Analyses: Fish samples will be cut into pieces, if needed, and mixed with dry ice or liquid nitrogen in a 1:1 ratio. The frozen fish sample will be homogenized in a Blixer stainless steel blender and subsampled for extraction using accelerated solvent extraction (ASE). Dichloromethane and ethyl acetate are solvents that are likely to be used for the ASE extraction. Sodium sulfate will be used to remove water from the matrix. Because the co-extracted fish lipids will interfere with the GC/MS analysis, lipids will be removed during the ASE extraction procedure by packing sulfuric acid-impregnated silica in the bottom of the ASE cell as a fat retainer (Bjorklund et al., 2001) or by treating the ASE fish extracts with 9 M or 18 M sulfuric acid prior to analysis (Berdie and Grimalt, 1988; Wang et al., 1999). If the target analytes are degraded during both of these procedures, gel permeation chromatography (GPC) will be used to remove lipids from the extracts prior to analysis (Lazar, 1992). If needed, further extract purification will include silica or alumina column chromatography. The percent moisture and lipid content of the fish samples will be measured.

Histopathology: Slides will be prepared at the EPA Gulf Breeze laboratory or the OSU Schreck laboratory. Tissue specimens in labeled cassettes will be dehydrated, cleared, and infiltrated with Paraplast paraffin. Representative sections will be cut from each tissue specimen with a microtome. Sections will be cut at 6 microns, floated on water, and captured on microscope slides dried at 48^{o} C overnight. Two slides containing 2 to 5 sections each will be prepared from each specimen. Histological slides will be stained with Harris' hematoxylin and eosin (H&E). Following staining, slides will be coverslipped for routine histological examination. Macrophage aggregates will be calculated with SPOT software. All slides will be read by both Drs. Kent and Fournie, and results shared only after both have read the slides independently.

Physiology: Physiological examination of tissues (blood and others) is determined by competition binding assays, including radioimmunoassays and enzyme-linked immunosorbant assays (ELISA), or colorimetric assays in which the degree of color change is determined by spectrophotometry. Concentrations are calculated from a standard curve prepared for each batch of samples. The sensitivity and working range of all competitive binding assays are empirically determined. Frozen plasma is thawed and assayed for vitellogenin by ELISA, sex steroids (estradiol, testosterone, 11-ketotestosterone, 17α, 20βdihydroxyprogesterone,) by radioimmunoassay, and cortisol by radioimmunoassay. Glucose is determined using a Nova Biomedical Blood Analyzer.

Scales and Otoliths: Sagital otoliths will be prepared by slide mount in epoxy and ground and polished in the transverse plane. Otoliths will be ground until the core is visible with the sulcus facing up, flipped, and ground similarly with the sulcus down. Annuli are examined under transmitted light microscopy. Otoliths are examined randomly and age recorded until agreement between readings is reached.

5.8 Quality Control Procedures

5.8.1 Field Procedures

Fieldwork will follow established protocols involving fish capture and sample collections throughout the entire process. Information regarding fish species, age, sex, general health condition will be recorded on prepared data sheets. Labels are filled out with permanent marker and will be permanently fixed to all containers of fish tissues. All original data sheets will be carried as personal baggage during transit and photocopied and kept in separate locations as soon as facilities permit.

All observations of fish and fish tissues must be consistent so evaluation of and comparisons between sites are reliable. It will be important for fish to be examined independently, without prior knowledge of contaminant burdens or collaborating pathologist interpretations. Within sites, the same person will make evaluations. All researchers that will conduct macroscopic health evaluations will be trained by Dr. Kent prior to field trips to optimize consistency. In addition, a digital image of unusual macroscopic changes will be made.

Balances used for fish weight will be checked for consistency and accuracy using a calibration weight set. A range of calibration weights will be measured and recorded prior to weighing sample fish.

5.8.2 Laboratory Procedures

Histopathology involves subjective evaluations of tissues by trained pathologists. All lesions will be confirmed by independent evaluation of the two pathologists on the project. Dr. Kent will interpret histological slides from all fish. All positives (along with a mix of negative tissues) will be sent to Dr. Fournie, EPA Gulf Breeze, for separate interpretations. Slides will receive a separate number and will be delivered to Dr. Fournie without Dr. Kent's results. After independent evaluations, Kent and Fournie will compare results, and a consensus diagnosis will be made.

Given that macrophage aggregates (MA) are affected by many factors (other then contaminants), an index needs to be established by which to compare MA in the sample fish. To be as accurate as possible, the fish used for the index should be exactly the same as the sample fish. Therefore, we will use sample fish that are "contaminant free" to establish the index. This procedure is assuming that some of the sample fish will have no contaminant body burden. This procedure was used by the EMERGE group.

Inter-assay variation is assessed by plasma pools with a known amount of steroid added. The plasma pool samples are run in triplicate at 2 dilutions. Experimental samples are run in duplicate or triplicate within a given assay to determine the intra-assay variation. These measures are performed every time an assay is performed.

For the Nova Analyzer, analytes of interest (e.g., glucose) are purchased from the manufacturer with a known amount of analyte added for quality control purposes. The known sample from the manufacturer is run side-by-side with the unknown experimental samples. The data from the experimental samples are used only if the said analyte falls within specified range of concentrations for the given lot.

The quality control data from each physiological endpoint is recorded to chart "drift" or any abnormality. Histological processing runs are charted similarly to physiology with log books recording all aspects of a particular sample run. This ensures that solutions are changed as required and equipment cleaned and properly maintained.

5.8.3 Interannual Variation

Fish will be sampled each year of the study from one lake in one of the parks to provide information on possible inter-annual effects. The lake selected for this sampling will be PJ Lake in Olympic National Park.

5.8.4 Preventive Maintenance Procedures And Schedules

Weekly/daily observations will be made of all instrumentation related to the execution of endpoint methodologies to determine the operational status of such equipment. Preventive procedures and required repairs will be performed by project staff or technical service

representatives to maintain this equipment in operational order as deemed necessary by routine inspections by the research staff. Service contracts are used to be sure that equipment is maintained by qualified technicians trained by the manufacturer.

5.8.5 Corrective Action

If problems are noted with any aspect of data or sample quality, the Project Leader will contact the WACAP Program Director and Drs. Kent and Schreck and inform PIs of the problems encountered and suggest corrective action appropriate to problem(s).

5.9 Data Management

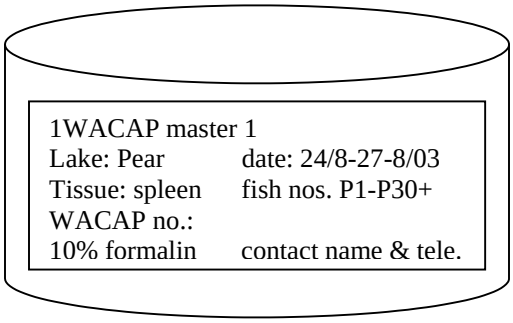
Since WACAP is a multi-year project, sample labeling and data organization are critical as large amounts of information will be obtained, stored, accessed by numerous individuals. Therefore, the following strategy will employed for duration of the study.

1. A small "Rite in the Rain" field journal will contain anecdotal information re: weather, net setting, sampling locale, fishing report, etc.
2. Data will be organized in laboratory notebooks with carbon copies. After completion of a round of data entry, the carbon copy will be removed and stored in a separate location of the original.
3. Lab books will be numbered consecutively with the following scheme: 1 WACAP master 1,2 etc.; 1 WACAP steroid 1,2 etc.; 1 WACAP Vg 1,2 etc. and so on for all analyses. The "1" preceding WACAP will represent year (sampling) of the study. The numbers following the words represent the number of books required for that year of data.
4. The "master" will contain all data recorded in the field. The other analyses will refer to the master so that the fish number will be easily matched with corresponding parameter. A WACAP sample number will be assigned according to the plan described in section 13.2. The "master" will be on "Rite in the Rain" (waterproof) paper in the below format.

Date	Time	Lake	GPS		Crew		Pg. 1
24-8-03	14:30	Pear					
Fish no.	WACAP no.	Fk lgth	Beg mass	End mass	Sex	devl stage	yr cls
P1	36161	15	86	80	M	Im	0

5. Macroscopic health index measurements will occur during initial sampling as the tissues are being removed and recorded on "Rite in the Rain" paper.
6. The following lab books will refer to the "master" by citing the fish number dash page number. For example steroid assay samples will be labeled P1-1, P2-1, P3-1 and so on until page 2 where the label will read P32-2, P33-2. Each assay will also refer to "master" by citing which master the samples came from. Redundancy in this system is employed to be sure that anyone can read the lab book and understand.
7. Fish will be labeled with a tag placed inside Ziploc but not in foil.

8. Frozen tissues and cassettes containing fixed tissues will be labeled with fish number. Slides and assay vials will refer to fish number and page number as above. Sample jars (fixed tissue) and boxes (frozen tissue) will be kept separate for each lake and be labeled as below.



9. Below are parks, lakes, and lake abbreviations to be employed throughout the study.

PARKS	LAKE / Abbreviation		
Rocky Mtn	Mills / ML	Lone Pine / LP	
Sequoia	Pear / P	Emerald / E	
Denali	Wonder / W	McLeod / MC	Foraker / F
Noatak	Burial / B	Desperation / D	
Gates	Matcharak / MA		
Olympic	Hoh / H	PJ / PJ	
Rainier	Mowich / MO	Golden / G	LP19 / L
Glacier	Snyder / S	Oldman / O	

Pertinent data of histological observations are recorded on histological record forms and maintained in appropriate log books. Physiology raw data is recorded in laboratory notebooks with carbon copies and stored in 2 locations. Diagnostic information is also stored in computer files referenced through histological record codes. Physiological endpoints are entered into spreadsheets and backed up on floppy and compact discs. Information entered into computer files will be checked against hard copy records for accuracy. Digital images and printed hard copies of microscopical data are obtained as using SPOT digital camera systems equipped on both Dr. Fournie's and Dr. Kent's microscopes.

6.0 Vegetation

Vegetation samples collected from WACAP sites will include lichen, willow bark and conifer needles. SOC analyses will be conducted on lichen, willow bark, or conifer needles, depending on the results of preliminary samples collected in 2003. All three vegetation types will be collected in 2004 from the 8 WACAP Parks, but only one type will be used for SOC analyses. In addition, lichen samples will be collected for analyses of nitrogen, sulfur, metals, and mercury. Additional samples for SOC analyses (of the vegetation type determined to be best for SOC analyses), may be collected from up to 12 National Parks in 2005.

6.1 Introduction

Chemical analysis of contaminant levels in lichen tissue will provide a present-day assessment of metals, sulfur, and nitrogen levels in the parks. This information will make it possible to evaluate whether metals, sulfur or nitrogen should be considered a concomitant stress in analyses of other matrices. We anticipate that lichen analysis can corroborate some contaminant signals or combinations (i.e. ratios) of signals from sediment data that will enable us to link impacts in some catchments to trans-Pacific air masses if such impacts exist.

Because air pollutants, climate, elevation, and proximity/exposure to emissions sources differ among the watersheds, contaminant content is expected to vary somewhat among watersheds. Factors influencing lichen contaminant content include lichen species, topographic exposure, frequency and duration of precipitation events, temperature ranges, presence or absence of winter snow cover, deposition rates, thallus age, and pollution chemistry. Yet analysis of lichens from the Pacific Northwest and Alaska has shown that tissue concentrations of elements within a single lichen species from clean sites are quite similar and significantly lower than element concentrations in the same species collected from urban, industrial and agricultural environments. This is despite the fact that the forests span a wide range of altitudes, climatic extremes, and experience large differences in rainfall, humidity, and temperatures, from the temperate coastal rainforests to dry, cold, continental forests

To maximize data comparability, we will use the minimum number of species to achieve greatest overlapping within and across parks. The sulfur, nitrogen and metals data we obtain will be compared to other data for the same lichen species from known clean or polluted sites within the same regions and broader areas. Within a watershed, our objective will be to identify average values for contaminants within the lichen population. To do this we will collect many individuals from the range of exposures and microhabitats in the watershed, and collect three field duplicates of each species.

Our objective will be to identify average values for contaminants within the lichen population of each watershed, and then assess whether these values are higher than those at known clean sites, and assess the ecological implications of the findings. We expect to estimate the degree of loading of nitrogen and sulfur to the target watersheds by comparisons with “local” monitoring stations. Except for Mt. Rainier and Sequoia, these levels are expected to be within natural, historic ranges, and unlikely to impact sensitive species. We also plan to compare results from the WACAP parks to other sites in the western US and Canada, primarily on

federally managed lands, and to places in Europe and Asia that have been studied using the same species. Findings will be integrated with other indicator matrices, for example to calculate bioconcentration factors, and indicate potential synergistic stresses from metals, and sulfur and nitrogen containing pollutants.

Vegetation is recognized as a good qualitative indicator of atmospheric contamination of lipophilic SOCs and can be used to assess regional and even global variation in atmospheric contamination levels. Several studies have used tree bark to assess regional and global atmospheric contamination levels of polycyclic aromatic hydrocarbons (Simonich and Hites, 1994a), organochlorine pesticides (Simonich and Hites, 1995a; Simonich and Hites, 1997) and polychlorinated dibenzo-*p*-dioxins and furans (Wagrowski and Hites, 2000). Tree bark was used for these studies because it is present globally and has a relatively high surface area and lipid content (Simonich and Hites, 1995b). In addition, tree bark remains on most trees for several years and integrates the atmospheric concentration of lipophilic SOCs over this time period (Simonich and Hites, 1995b).

Willow bark (*Salix*) has been chosen as a matrix in this study because it is present throughout the selected Parks, grows at relatively high elevations, and is part of the terrestrial food-web within the Parks. If willow bark is found to be a poor accumulator of SOCs, conifer needles or lichens will be used instead. Compared to willow, conifers are less likely to be present in arctic and alpine ecosystems, however conifer needles have been used as qualitative indicators of atmospheric SOC contamination in high elevation ecosystems (Davidson et al., 2003). Lichens are available at all elevations and obtain most of their nutrients from atmospheric gases and deposition. Recent improvements in instrumentation and methodology have made analysis of lichens feasible, and lichens have been found to be comparable or better accumulators of a variety of SOCs compared to other plants (Calamari et al., 1991; Morosini et al., 1993; Muir et al., 1993) and even some animal tissues (AMAP, 1997; Jensen et al., 1997). The lichen, *Letharia vulpina*, collected by WACAP researchers in Sequoia National Park in 2003, was found to have detectable amounts of all analytes tested. However, to date, no comparisons have been made by WACAP researchers between lichens, willow and conifer needles collected at the same sites.

6.2 Sample Collection for SOC Analyses

6.2.1 General Sampling Procedures

Vegetation samples are to be collected at five elevations within a National Park. Ideally collection sites will be well-exposed and be selected at 500 meter intervals. If other WACAP matrices are being monitored within the Park, then the five sites should be within the same quadrant of the Park in which the target lakes are located and two of the collection sites should be within the target lake watersheds, ideally within 1-2 km of the lakes. In the arctic and for parks with a small elevation range, collectors may choose to put collection sites at smaller elevation intervals, or they may decrease the number of collection sites. The minimum number of collection sites is three, and the minimum elevation interval is 150 m.

The sampling site should be at least 0.4 ha (a circular plot of ~37 m radius) and generally not more than 1 ha in size. Sampling should be dispersed within and representative of the

sampling site. In 2004, all three vegetation types will ideally be collected at each of the five vegetation sampling sites. If not, establish a secondary sampling site(s) nearby to obtain the missing vegetation type(s). Complete separate field data cards at each sampling site, including secondary sites.

All vegetation samples will be collected into metalized, polyester Kapak© bags (Kapak Corporation, 5305 Parkdale Dr., Minneapolis, MN 55416, Product No. 606B-500S). The filled bags are sealed tight by folding the open edge down three times, then sealing the folded edge and sides of bag with ¾ to 1" wide, removable, laboratory tape. The bags can be made air-tight when they are $\leq$ 2/3 full. Use additional Kapak bags for larger samples. Sample weights are measured using a 100 g Pesola© spring scale. Sample weights in the following sections do not include the weight of the Kapak bag (7.5 g). Information to be recorded on the Kapak bag (see willow bark, conifer needles and lichen sections below) is written with a medium tip indelible marker, such as a Sharpie©, directly onto the Kapak bag, after the bag has been sealed, and on the taped side. Do not write on the tape itself as this must be removed to inspect, clean, or use the sample.

Field Equipment

The following is a checklist of the supplies needed to sample vegetation. All materials except the coolers, lichen drying kit, aluminum foil, and extra supplies are carried in a daypack during sampling. The coolers, packed with ice or dry ice, are left at base camp; samples are placed in the coolers within 12 hours of collection. The aluminum foil is used at base camp to re-wrap solvent washed knives and garden snips, and as a surface area for processing conifer needles.

Work Supplies

- Wrist or pocket watch
- Hand lens,15-20x
- Hand-held Global Positioning System (GPS)
- Detailed topographic maps, with elevation contours and hiking trails.
- 'Rite in Rain' field notebook
- No. 2 pencils, fine-tip and medium-tip blue or black Sharpies
- Copies of field protocols and Vegetation Field Data Card on "Rite in the Rain" paper
- Identification books for trees & shrubs, other vascular plants, lichens
- Gallon-sized Ziploc bags, one bag for each sample to be collected
- Orange plastic flagging
- 50 meter tape measure
- Sample Collection Supplies. The following materials are to be stored in one large Ziploc bag:
    - ¾" to 1" wide laboratory tape, 1-2 rolls
    - Medium-tip Sharpies, 2
    - Pesola spring scale, 100 g, in plastic case
    - Kapak bags folded in half inside a clean Ziploc bag, one per sample
    - Nitrile gloves, in a clean sandwich-sized Ziploc bag, 20 gloves
    - Solvent-washed garden pruners (Felco #2), wrapped in aluminum foil, and placed in a sandwich-sized Ziploc bag

    - Solvent-washed folding knife, wrapped in aluminum foil, stored in a sandwich-sized Ziploc bag
- Plastic garbage bags stored in a clean Ziploc bag, 1 per sample
- Twist-ties for sealing garbage bags, 1 per sample
- Pole pruners (not needed in Alaska parks).
- Paper lunch sacks for willow vouchers, 2-3 per sampling site
- Several large, plastic coolers for samples, with ice, preferably dry ice.
- Lichen drying kit. A large Ziploc bag containing 12-15 new wooden clothespins, a 20 m clothesline, 12-15 solvent washed nylon mesh bags wrapped in aluminum foil and stored in a sandwich sized Ziploc bag, twist ties, thirty 100% cotton 5 X 5 cm labels with a hole punched through them and a glued on hole reinforcer.
- A clean roll of heavy-duty aluminum foil, stored in a clean plastic bag.
- Extra Kapak bags, garbage bags, tape, nitrile gloves, twist-ties, and Ziploc bags (gallon & sandwich size)

Safety/personal

- Radio or cell phone (maintain daily communications)
- Matches in waterproof case, and candle or firestarter
- Sheathed or folding knife
- Head-lamp
- First aid kit
- Whistle
- Compass
- Altimeter (remember to reset each day)
- Extra clothes in anticipation of stranding or weather change (wear long pants, long sleeve shirts, sturdy waterproof boots, hat)
- Water
- Lunch and extra snacks
- Rain gear
- Extra batteries for the radio and GPS
- Insect repellent
- Sunscreen
- Sunglasses
- Cell phone charger (if appropriate)
- Garbage sack (bright orange)
- Ear plugs (Alaska only)
- Headnet

What to Record

The following information should be recorded on the Vegetation Field Data Card (Figure 6.2.1) at each site using a pencil or fine-tip indelible marker:

Date/Time. Day, month, year, and time at the collection site (e.g., 3-5 PM).

Figure 6.2.1 WACAP Vegetation Field Data Card 2004

Record the following information at each sampling site. Use a pencil or indelible marker.

1. Sampling Site No. _____ Use the Park 4-letter acronym (SEKI, MTRA, OLYM, GLAC, ROMO, DENA, NOAT, or GAAR) followed by a digit (1-5) to denote position from lowest to highest in the elevation gradient. If there is more than one sampling site per elevation, for example different sites were selected for EA vs SOC collections or willow vs lichen, follow the number with a letter, e.g. DENA1a.

2. What was collected? Include vegetation samples for SOC & Element Analyses (N, S, metals).

	Species collected	*Rep*	*Wt (g) w/o bag*	*SOC or EA?*	*Lichens Only*	
					Substrate	*Moisture status (dry, damp, wet)*
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						

3. Date/Time at site. (e.g., 7 July 2004, 3-5 PM). _____ . Record approximate time (min) needed to collect **willow** _____, **needles** _____, **lichens** _____ .

4. Name of collector(s). Write full first and last name_____

5. Location description. Someone with a general park map should be able to find the approximate location of the sampling site from this description. If a target watershed, record the name of the lake.

_____

_____

6. Location coordinates. Measured by GPS at sampling site center. Use mapping datum WGS84 and 'geographic' projection. If WGS94 is not available, record the mapping parameters you used.

*Latitude N (*decimal degrees*)* _____ *Measurement accuracy* (m) _____

Longitude W (decimal degrees) _____

Figure 6.2.1 WACAP Vegetation Field Data Card 2004 (continued)

7. Elevation at center of sampling site_____**Units (circle one): m / ft**. Record in meters if GPS or altimeter are accurate to 25 m, otherwise record in units provided by the topographic map. If elevation of the sampling site varies >35 m (100 ft) from the mean, record min _____ and max_____ .

8. Sampling area radius (m)_____. If the sampling area was roughly circular, record the approximate radius of the area that was sampled. Otherwise, estimate length _____ and width _____. Values recorded should be accurate within +/- 35 m.

9. Mark the map. Delineate the boundaries of the sampling area on the topographic map. Mark the map with the 'Sampling Site No. *Is map marked?* (Circle one) YES ? NO

10. Habitat/ Remarks. Describe the including vegetation type (forest, woodland, tundra, etc.), tree ages (if known), stand height, stand structure (presence of multiple age classes). Record deviations from standard operating procedures, weather conditions—especially very warm or very wet conditions, any unusual features in or activities near the site, any remarks about the samples or their condition.

_____
_____
_____
_____
_____
_____

11. Vegetation cover. Record names of dominant and indicator species in the appropriate box. For lichens/bryos put an 'X' in the appropriate box to indicate ground cover of lichens and bryophytes.

Cover:	0-5%	6-25%	26-50%	51-75%	76-100%
Trees/shrubs					
Forbs/grasses					
Lichens/bryos					

12. Physical characteristics.

Exposure (circle one): full sun, partly shaded

Aspect (degrees) _____

Slope (%) _____

Landform (circle one): valley, flatland, toe slope, mid-slope (1/3-2/3), upper slopes (top 1/3), ridgetop

13. Sample Processing, Drying, Storage. Record when the samples were placed on ice. Also record when the conifer needles were processed, and if the lichens were dried on site, when that happened, how they were dried.

Process	*Date*	*BeginTime*	*End Time*	*Notes*
Dry wet/damp lichens				
Clip/strip conifer needles				
Samples placed on ice				

Name of collector(s). Write full first and last names.

Collection Site. One or two words describing the collection site (e.g., the name of a nearby lake or stream, or other topographic feature).

Location description. One sentence. Someone with a general map of the park should be able to find the approximate location of the collection site from this description.

Location coordinates. At the center of the collecting area. (record latitude, longitude, UTM zone, Easting, Northing). Use mapping datum WGS83 and a GPS, most instruments can toggle between units of measurement.

Elevation. At the center of the collecting area. Record in meters if GPS or altimeter are accurate, otherwise record in units provided by the topographic map.

Sampling area. Describe the approximate area that was sampled (in ha).

Habitat. This is a description of the vegetation on the site, includes such notes as tree types, ages (if known), vegetation type (forest, woodland, tundra, etc., stand structure (presence of multiple age classes) other dominant or indicator species.

Physical characteristics. Describe the exposure, slope, landform, rock types if saxicolous species are collected. Record % exposed soil or bare rock.

Remarks. Record any deviations from standard operating procedures, weather conditions—especially very warm or very wet conditions, any unusual features in or activities near the site, any remarks about the samples or their condition.

Sample Processing, Drying, Storage. Record when the samples were placed on ice. Also record when the conifer needles were processed, and if the lichens were dried on site, when that happened, how they were dried, and how long the process took.

Mark the map. Delineate the boundaries of the sampling area on the topographic map. Mark the map with the 'Location name".

6.2.2 Willow Bark

Because willow bark is ubiquitous throughout the parks, it will be possible to collect samples from multiple sites within a given park and among parks. Willow bark has the distinct advantage in that it is easy to collect and carry out of a park, but the disadvantage of not being present at the highest elevations within some parks and being closely associated with protected riparian corridors in other parks. If willow bark is determined to be a good matrix for SOC analyses, it may be possible to have additional parks, not originally included in this study, collect willow bark samples.

Willow bark stems will be collected in ~25 cm lengths using nitrile gloves and a clean pair of garden snips. One sample would be the equivalent bark volume of 10 stem segments of 2-2.5 cm diameter, with stems sampled from multiple plants. Three field samples will be collected per site. The willow stems will be placed in air-tight, metalized polyethylene Kapak bag (see Section 6.2.1 General Sampling Procedures for sealing protocol). On the outside of each sealed sample bag record:

- Unique sample number (can be done later in camp or in the lab, use pre-assigned WACAP numbers in Figure 13.1)
- Park 4 letter acronym
- Sampling Site No. (Use the same name recorded on the field data card.)
- Elevation. Record units.
- Willow genus and species. If identification is not possible, collect a separate voucher into a paper bag for identification by a park botanist. Ideally the voucher should contain leaves, bark, flowers and fruits. Mark the location name on the outside of the bag.
- Field replicate number (1, 2 or 3)
- Collectors initials and date

Analytical method development is underway, using field samples collected during the summer 2002 from Desperation and Burial Lakes in Noatak National Preserve and Matcharak Lake in Gates of the Arctic National Park. Additional samples were collected from an elevational transect in Banff National Park (Alberta, Canada). The willow bark stems will be aged by counting the growth rings and lipid content will be measured in all samples.

6.2.3 Conifer needles

Conifer needles are collected by snipping terminal branchlets of at least 3 years growth into a large plastic 'garbage-sized' bag. Collectors will wear nitrile gloves and use garden snips cleaned with an organic solvent in the laboratory. When not in use, garden snips will be wrapped in aluminum foil and stored in a clean Ziploc bag. About 2-3 kg of conifer branchlets should be collected. Note that there are more first year than second year segments on each branchlet—and adjust field collecting as necessary, as the same final weight is needed for both segment types. Preferred conifer genera are *Abies*, *Pinus*, *Pseudotsuga*, and *Tsuga*. One genus is to be sampled at each collection site. Highly preferred species are Engelmann spruce (*Picea engelmannii*), lodgepole pine (*Pinus contorta*), white spruce (*Pinus albicaulis*), and whitebark pine (*Picea glauca*). If in doubt about the species name, collect a voucher of branchlets and cones in a paper sack for later verification. Label with the Sampling Site No.

The same day of collection, using cleaned garden snips and wearing nitrile gloves, the branchlets are snipped and sorted into first and second year segments using the terminal bud scar as a marker. This operation must be done in the daylight because adequate light is required to see the bud scar. A clean flat place, near camp but not close to generators or cooking facilities is best. Work can be done inside a tent if mosquitoes are bothersome. The 1- and 2-year branch segments are placed in separate piles on clean sheets of aluminum foil. The needles are then stripped from the woody parts and packaged into clean metalized polyester Kapak bags. Clipping and stripping is continued until 3 replicates of 50 g each have been obtained for both 1- and 2-year segments of each tree species. If time is limited, package the samples without stripping needles from their stems, adding extra material to account for the combined weight of the stems. Seal the Kapak bags (see Section 6.2.1 General Sampling Procedures for sealing protocol) and record the following on each sample:

- Unique sample number (can be done later in camp or in the lab, use pre-assigned WACAP numbers in Figure 13.1)
- Park 4 letter acronym

- Sampling Site No. (use the same name recorded on the field data card)
- Elevation. Record units.
- Conifer genus and species
- Branch segment year
- Field replicate number (1, 2 or 3)
- Collector's initials and date

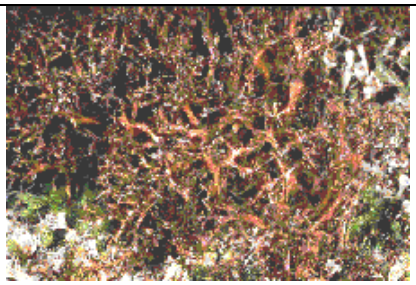
6.2.4 Lichens for SOC Analyses

Lichens are collected into Kapak bags using nitrile gloves. See Figure 6.2.2 for preferred target species. Ideally, just one lichen species should be collected at all elevations in the park. Collect one species, choosing the species by balancing preferred status in Table 6.2 versus ease of collection at the sampling site. If none of the target lichens are present, choose a different location. It may be necessary to use pole-pruners to reach epiphytic lichens in areas that have deep winter snow. If it is not possible to collect epiphytic lichens directly from branches, they may be collected from the litter as long as they are recently fallen, free of debris, and in good condition. For terricolous lichens, collect only above-ground parts. Saxicolous lichens should be carefully removed from their rock substrates with a knife that has been cleaned using a solvent wash. Brittle, crumbly, faded or discolored lichens of all growth forms should be avoided. Samples are to be collected at least 50 m away from minor dust sources such as foot or pack animal trails, or dirt roads—and at least 100 m away from larger sources such as well-used roads, construction sites, and other high use areas or facilities. Collect three 20 g (dry weight) lichen samples at each sampling site. Lichens will not be processed further before SOC analysis, therefore they should be as free of extraneous debris, other lichen species, and bark, as possible. Each sample should represent a minimum of eight different trees (epiphytes) or locations in the sampling area (terricoles and saxicoles). Seal the bags and record the following on each bag:

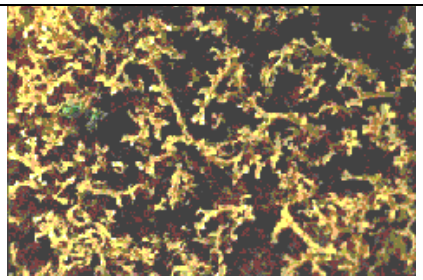
- Unique sample number (can be done later in camp or in the lab, use pre-assigned WACAP numbers)
- Park 4 letter acronym
- Sampling Site No. (use the same name recorded on the field data card)
- Elevation. Record units.
- Lichen genus and species
- Field replicate number (1, 2, 3, or 4)
- Collector's initials and date
- Moisture status of sample (dry, damp, or wet)

Wet lichens are about 10 times heavier than dry lichens and decay rapidly in sealed plastic bags, unless kept very cold. *If at all possible, lichens should be collected dry.* Dry lichens in a sealed bag will make a 'crunching' sound when squeezed gently; bags of wet or damp lichens are soft and noiseless when squeezed. If the lichens are damp, and they cannot be kept on dry ice, or cannot be delivered to the laboratory within 24 hours, then they should be air-dried within 24 hours. To do this, transfer each damp or wet lichen sample into a solvent washed nylon mesh bag, twist tie shut, attaching a paper label containing the unique sample number, then attach with wooden clothespins to a clothes line strung up near base camp, but away from

cooking facilities and generators. Depending on conditions, lichens can be expected to dry in 2-24 hours.


Cetraria islandica


Cladina rangiferina


Flavocetraria cucullata


Hypogymnia physodes


Parmelia saxatilis


Parmelia sulcata


Peltigera aphthosa


Peltigera canina


Platismatia glauca


Umbilicaria hyperborea


Bryoria fuscescens


Flavocetraria nivalis


Peltigera leucophlebia

Figure 6.2.2 Potential WACAP target lichen species
Photographs, except *C. islandica* and *F. cucullata*, courtesy of S. Sharnoff

Table 6.2 Lichens at the Target Watersheds. Species in bold are preferred for tissue collection.

Park:	DENA	GLAC	GLAC	MORA	NOAT/ GAAR	OLYM	ROMO	ROMO	SEKI
Lake(s):	Wonder McLeod Foraker	Snyder	Oldman	Golden LP-19	Burial Matcharak Desperation	Happy Hoh	Lone Pine	Mills	Emerald Pear
Lichen	Habit								
Alectoria sarmentosa	epiphytic		**x**		**x**		**x**			
Bryoria fremonitii	epiphytic		x	**x**					
Cetraria laevigata	terricolous	**x**				**x**			
Cladina arbuscula	terricolous	x				x			
Flavoceteraria cucullata	terricolous	**x**				**x**			
Flavocetraria nivalis	terricolous	x				x		?	?	
Hypogymnia austerodes	epiphytic	x				x			
Hypogymnia enteromorpha	epiphytic		x				x			
Hypogymnia imshaugii	epiphytic		x						
Hypogymnia physodes	epiphytic	x	x			x			
Letharia vulpina	epiphytic			**x**						**x**
Peltigera aphthosa	epiphytic							**x**	**x**	
Parmelia sulcata	epiphytic	x			x	x			
Platismatia glauca	epiphytic		**x**		**x**		**x**			
Peltigera aphthosa	terricolous									
Umbilicaria torefacta	saxicolous		x							
Umibilicaria americana	saxicolous							x	x	
Umibilicaria hyperborea	saxicolous			x						
Usnea lapponica	epiphytic							**x**		
Xanthoparmelia coloradoensis	saxicolous							**x**	**x**	

6.3 Lichen Sample Collection for N, S, Metals, and Hg Analyses

Our target is to collect approximately 15 grams dry weight of one lichen species per sample. Three replicate samples of two lichen species will be obtained per watershed for a total of six samples. At 14 watersheds, this makes a total of 84 samples/year. Follow the procedures described in the section above for collection of lichens for SOC analyses. The primary difference between sampling for sulfur, nitrogen and metals and sampling for SOCs is that the lichens do not need to be kept cold. Each sample should contain a large number of individuals representing the various aspects and exposures in the watershed between ground level and arms reach.

6.4 Sample Transport and Storage

Damp lichen samples will be kept cool, then air dried in the field within 48 hours and repackaged. To air dry samples, lichens will be transferred to cleaned mesh bags and suspended from a clothesline at the field location. Surface debris, bark, and damaged parts of the lichen thalli, will be removed by hand. Air-dried lichen samples for S, N, and metals analysis will be mailed to the USGS Boulder Laboratory for further drying, grinding, and trace metals analysis (Figure 6.4). Aliquots of dried, ground lichens from each site will be shipped to the University of Minnesota Research Analytical Laboratory (UMNRAL) for nitrogen and sulfur analysis, and to the WRS Analytical Laboratory in Corvallis for mercury analysis.

Vegetation samples for SOC analyses will be stored cold or frozen (dry ice is preferred), and shipped as soon as possible (within 1-3 days) to the WRS Analytical Laboratory for storage in a freezer. Samples will be stored frozen and sealed until analysis at the Simonich Environmental Chemistry Laboratory.

6.5 Sample Preparation and Analysis

Laboratory methods for sulfur, nitrogen, and metals analysis will follow established methods and involve standard analytical instrumentation and techniques. See the UMNRAL website, http://ral.coafes.umn.edu/plant.htm, for more detailed descriptions of the following sample analysis procedures:

- Sample aliquots for separate analyses of sulfur and nitrogen are weighed after the ground lichen samples have been oven-dried at 65^{o} C to a constant weight.
- **Nitrogen** is determined by a LECO FP-528 Nitrogen Analyzer. The N analyzer combusts a 200 mg sample, converts the resulting NO_x to N_2, scrubs other combustion products, then measures total N using a thermal conductivity cell.
- **Sulfur** is determined spectrophotometrically using a LECO S144-DR Sulfur Determinator. This instrument combusts a 150 mg sample then measures evolved sulfur dioxide by infrared absorption. Both sulfur and nitrogen are reported as % dry weight.

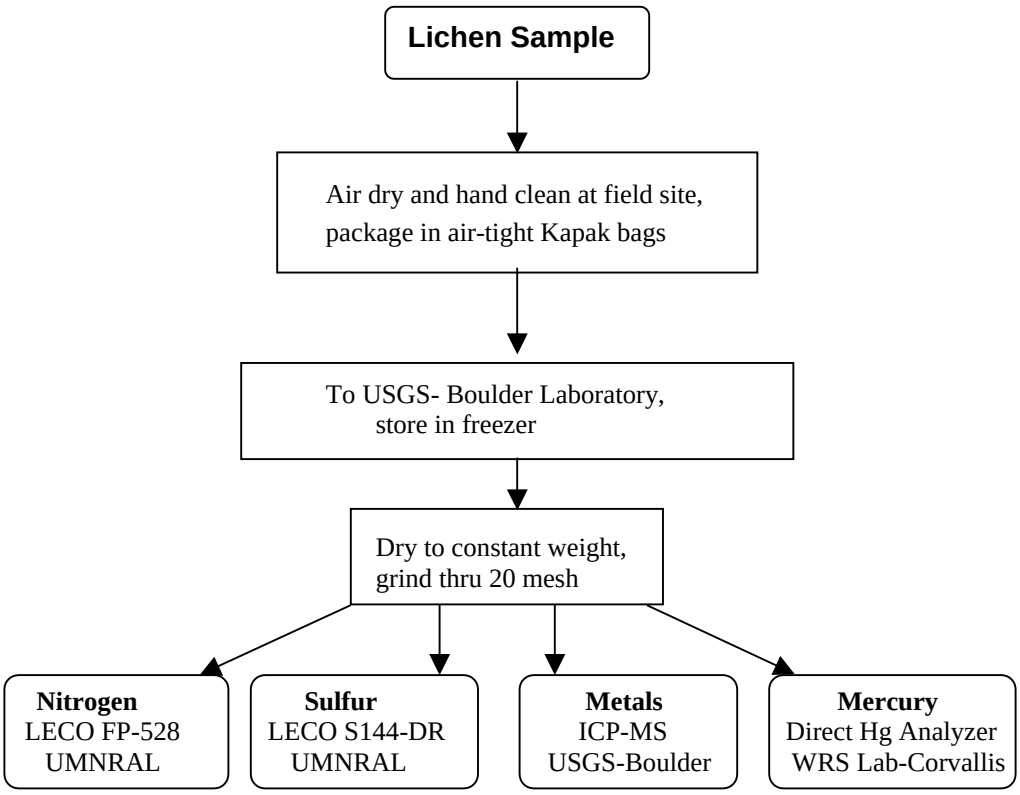


Figure 6.4 Lichen sample flow diagram

- **Metals (cadmium, copper, lead, nickel, vanadium, and zinc)** are determined by Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) at the USGS laboratory in Boulder, CO. Freeze-dried tissue samples are totally digested in a closed-vessel microwave oven procedure, using high purity nitric acid. After digestion, samples are diluted to volume with 1% high-purity nitric acid.
- **Mercury** is determined with a Milestone DMA-80 using a direct analysis method at the WRS Analytical Laboratory at EPA-Corvallis.

Analytical methods for SOC analyses are currently being developed using vegetation samples collected from Noatak National Preserve (Desperation and Burial Lakes) and Gates of the Arctic (Matcharak Lake) in the summer of 2002, and from Sequoia National Park (Emerald Lake) in the summer of 2003. Additional samples were collected from an elevational transect in Banff National Park (Alberta, Canada). Willow bark will be removed by dissecting it away from the stems using clean techniques and solvent washed implements (i.e. forceps, scalpel). The bark will be extracted using ASE, with a solvent system similar to the one used for the fish samples. ASE has been previously used to extract SOCs from vegetation samples (Wenzel et al., 1998). The extracts will be purified using silica or alumina column chromatography prior to analysis.

The percent moisture and lipid content of the willow bark samples will be measured. If the decision is made to measure conifer needles instead of willow bark, the analytical methods that are developed will also apply to conifer needles.

6.6 Quality Control

Field

The lichen indicator methodology will follow protocols already in use by the respective air divisions of the US Forest Service and National Park Service and will draw from baseline and thresholds lichen tissue data established by the USFS Air Program (http://www.fs.fed.us/r6/aq/lichen) and the Midwest National Parks Project (http://www.ies.wisc.edu/brd).

Sampling area and sample volume should be adequate to evaluate each target watershed. Triplicate lichen samples will be used to evaluate repeatability of estimates for each analyte and element within a watershed. Multiple samples will be collected and analyzed for SOCs within a given site. From these data, we will be able to calculate the variation in vegetation SOC concentration within each site and determine if any concentration differences measured between sites are statistically relevant. Field blank and laboratory blank experiments will also be conducted

Collection locations will be determined using GPS and stored as electronic waypoints in addition to being recorded in field notebooks and on topographic maps. Information regarding substrate, substrate location, sample condition, sample moisture status, drying history, and cleaning will be recorded on prepared data sheets. In addition, a digital image of each collection site (habitat) will be made. Vouchers of samples from each watershed will be collected, labeled, and stored in the lichen herbarium at the Siuslaw National Forest laboratory. Kapak bags will be labeled with site number, date, lichen species, substrates, moisture status, collectors name, and field weight. All original data sheets will be carried as personal baggage during transit and photo copied and kept in separate locations as soon as facilities permit.

Laboratory

Four laboratories will analyze vegetation samples collected from WACAP watersheds:

- University of Minnesota Research Analytical Laboratory (UMNRAL) will analyze nitrogen and sulfur in lichens in addition to drying and grinding the lichen samples.
- USGS Boulder Laboratory will analyze metals (except for mercury) in lichen
- WRS Analytical Laboratory will analyze mercury in lichen
- Simonich Environmental Chemistry Laboratory will analyze SOCs in willow bark, lichen, or conifer needles after method development and

Laboratory QA will include analysis of replicates, blanks, and a lichen standard reference material such as IAEA-336 (available from Analytical Quality Control Services, Agency's Laboratories, Seibersdorf , Austria). This information will allow us to assess laboratory accuracy

and repeatability, necessary for establishing significant differences between sample groups and accurately assessing accumulation of contaminants in lichens.

7.0 Subsistence Foods

7.1 Introduction

Subsistence food and its quality with respect to contaminants has been of great concern to the State of Alaska as well as the native communities which continue to use a wide variety of subsistence foods in their diets (Chary, 2000; USDI et al., 2000). WACAP is taking an interdisciplinary, ecosystem approach to evaluate and assess contaminants in ecosystems at risk for contaminants and we believe that including subsistence foods is a good way to make the connection to the human component of the ecosystem. This effort is not directly related to the overall goal and objectives of WACAP but it will provide an important link to the human subsistence component of the Alaskan foodweb.

7.2 Sample Collection

We plan to work with our NPS contacts to provide moose meat samples from individual moose killed by subsistence food hunters in Alaska and possibly Montana (Glacier National Park). Although sampling details may vary, we will need information on the location of the kill (elevation, latitude and longitude) and an approximate age of the animal. If possible, close proximity to WACAP sampling sites would be preferred and we would like samples from as many different parks as possible. The meat sample should be a single tissue sample that would be eaten by subsistence hunters (i.e. rump roast) of sufficient size (i.e. 5 lbs.) so that interior sub-samples can be taken by the analytical laboratory. Sample collectors should be careful not to contaminate the meat sample by human hands or unclean implements.

7.3 Sample Transport and Storage

Samples will be labeled with site location and collection date, and frozen solid at the park. Samples will be shipped in coolers to the WRS Analytical Laboratory in Corvallis by overnight courier.

7.4 Sample Preparation and Analysis

We expect that the analytical method developed for determining the SOC concentration in fish will also be applicable to the moose samples. The percent moisture and lipid content of the moose samples will be measured. Method development verification for the moose samples will begin in mid-Winter 2003.

7.5 Quality Control

Multiple samples will be sub-sampled and analyzed for metals and organic contaminants from each meat sample. From these data, we will be able to calculate the variation in contaminant concentration in moose meat within each sample and among sampling sites.

8.0 Surface Water: Water Quality Information

8.1 Introduction

Water quality data about the lakes in the WACAP catchments will provide basic information that will be used to characterize these ecological systems. The objective of the water quality component of WACAP is to characterize the condition of the WACAP lakes by assessing the chemical and physical characteristics of water quality, including trophic state, chemical contamination, and acidification. Lake characteristics will be used to help interpret information from other ecosystem indicators, such as sediments and fish.

We will follow water chemistry protocols from the Environmental Monitoring and Assessment Program's Surface Water (EMAP-SW) group. The EMAP program is planned and implemented by the U.S. EPA in cooperation with other federal and state organizations with the goal to monitor and assess the condition of the Nation's ecological resources and to contribute to decisions on environmental protection and management (Chaloud and Peck, 1994). The goal of EMAP-SW is to characterize the ecological condition of inland surface waters, and the water chemistry component contributes data that can be used to determine acid-base status, water clarity, primary productivity, chemical stressors, and nutrient status. WACAP will be collecting data from multiple indicators in the catchments, and it will be helpful to know basic ecological information, such as trophic status, as we interpret and relate data amongst multiple sources.

8.2 Sample Collection

We will follow the EMAP-SW sampling protocols for the water chemistry indicator by collecting a bulk water chemistry sample, and by measuring *in situ* variables such as specific conductance, dissolved oxygen, and temperature. The EMAP-SW analytes and their detection limits are listed in Table 8.1. These measurements will be collected at the same time as the fish sampling, during summer or early fall. The water chemistry sample will be collected at a depth of 1.5 m, from the deepest area of the lake, with a 2-L Kemmerer sampler, and stored in a 4-L cubitainer. Syringe samples will be collected from a port in the Kemmerer for closed system analyses of pH and dissolved inorganic carbon. A portion of the sample will be filtered with a hand pump through a glass fiber filter for chlorophyll analyses. The field collection form is shown in Figure 8.1.

8.3 Sample Transport and Storage

The cubitainer, syringes, and filter will be stored on ice in a cooler, and shipped via overnight FedEx as soon as possible after collection to the WRS Analytical Laboratory. The water samples will be collected on the last day of the fish sampling work to minimize the holding times. The water chemistry analytes have holding times that indicate the maximum length of time between sample collection and analyses that should be allowed and still maintain the integrity of the analyte. The holding times range from 48 hours to 6 months. WACAP lake sites

Table 8.1 EMAP-SW analytes, methods, and detection limits

Analyte	Method[1]	Detection Limit[2]
Specific Conductance	EPA 120.6; US EPA (1987)	NA
Temperature	US EPA (1987)	NA
Dissolved Oxygen (DO)	US EPA (1987), YSI Model 6920 Datasonde	NA
Turbidity	YSI Model 6920 Datasonde	0.1 NTU
pH (syringe, closed system)	US EPA (1987)	NA
Acid Neutralizing Capacity (ANC)	EPA 310.1 (modified), US EPA (1987)	NA
Chlorophyll a	APHA (1989)	1 µg/L
Total Suspended Solids (Residue)	EPA 160.2; APHA (1989)	0.1 mg/L
True Color	APHA (1989), EPA 100.2 (modified), US EPA (1987)	NA
Dissolved Organic Carbon (DOC)	EPA 415.2, US EPA (1987)	0.1 mg/L
Dissolved Inorganic Carbon (DIC), syringe, closed system	US EPA (1987)	0.1 mg/L
Ammonium (NH_4)	Lachat 10-107-06-3-D	2 µg/L
Nitrate + Nitrite Nitrogen	EPA 353.2	1 µg/L
Silica (SiO2)	EPA 370.1 (modified), U.S. EPA (1987)	5 µg/L
Total Dissolved Nitrogen (TDN)	EPA 353.2 (modified), US EPA (1987)	10 µg/L
Total Dissolved Phosphorus (TDP)	EPA 365.1 (modified), US EPA (1987)	2 µg/L
Chloride (Cl)	EPA 300.6; US EPA (1987)	0.03 mg/L
Nitrate (NO_3)	EPA 300.6; US EPA (1987)	0.03 mg/L
Sulfate (SO_4)	EPA 300.6; US EPA (1987)	0.05 mg/L
Calcium (Ca)	EPA 215.1; US EPA (1987)	0.02 mg/L
Sodium (Na)	EPA 273.1; US EPA (1987)	0.02 mg/L
Potassium (K)	EPA 258.1; US EPA (1987)	0.04 mg/L
Magnesium (Mg	EPA 242.1; US EPA (1987)	0.01 mg/L

[1] American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Seventeenth Edition. American Public Health Association, Washington, D.C.

U.S. EPA. 1983. Methods for Chemical Analysis of Water and Wastes. Environmental Monitoring and Support Laboratory. EPA/600/4-79/020, U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati.

U.S. EPA. 1987. Handbook of Methods for Acid Deposition Studies: Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

[2] The method detection limit is determined as a one-sided 99% confidence interval from repeated measurements of a low-level standard across several calibration curves.

WESTERN AIRBORNE CONTAMINANTS ASSESSMENT PROJECT

Inorganic Water Chemistry: Field Collection Information Page _____

Park/ Site	Sampling Date	Sample Type	Lab Sample No.	Samples Collected	Chl a mls filtered	DO (%sat)	Depth (m)	Temperature (°C)	Sp.Cond. (µS/cm) at 25°C
		R or DUP		____ 60 ml syringe: pH ____ 60 ml syringe: DIC ____ cubitainer sample ____ chlorophyll filter					
		R or DUP		____ 60 ml syringe: pH ____ 60 ml syringe: DIC ____ cubitainer sample ____ chlorophyll filter					
Sampling Location:									
Calibration Data: DO: elevation = _____ mmHg =_____				Specific Conductance:					
Notes:									

Figure 8.1 WACAP Inorganic Water Chemistry Field Collection Form

are in remote areas, and we anticipate that it will take at least one day to get a water sample to a FedEx shipping location.

8.4 Sample Preparation and Analysis

The bulk cubitainer sample is split into aliquots at the WRS Analytical Laboratory, following the sample preparation and preservation protocols for each analyte. Figure 8.2 shows the sample aliquots prepared from the bulk sample, with holding times and preservation methods. The chlorophyll filters are stored in the freezer.

8.5 Quality Control

The EMAP-SW sample will be collected during the site visits for fish and sediment sampling. Two Parks will be visited the first two summers, and three Parks will be visited in the third summer. A field duplicate will be collected from one site in each Park. Even though there will only be four to six samples each summer from WACAP, once the samples are received at the WRS Analytical Laboratory, they will be in regular EMAP-SW sample batches, which follow a regular schedule for analytical duplicates and filter blanks. The WRS Analytical Laboratory follows verification procedures and data validation procedures, including cation-anion balances, before releasing the data. Please see the Quality Assurance Plan for the WRS Analytical Laboratory for details of the quality assurance and quality control procedures that will be followed for the water quality samples.

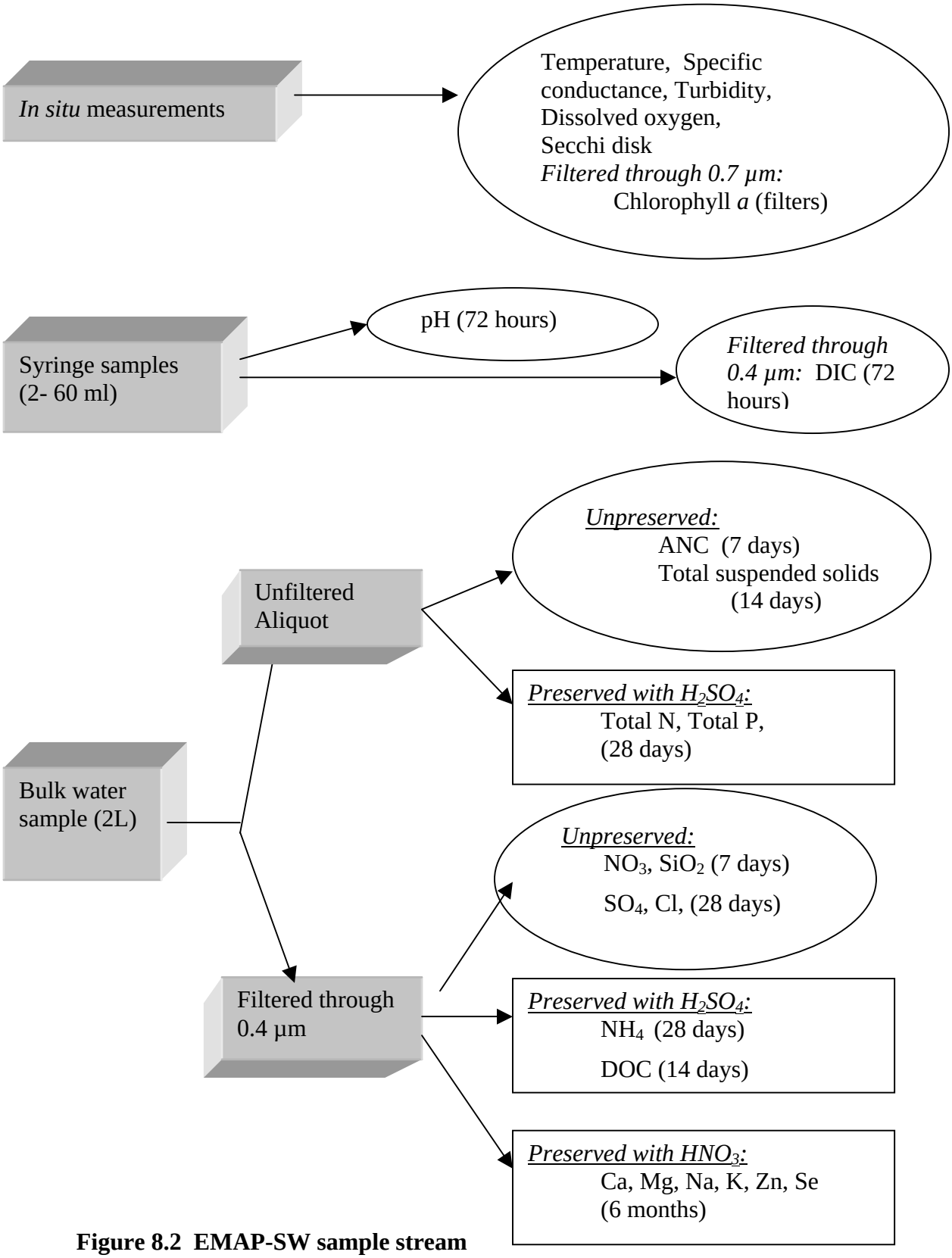


Figure 8.2 EMAP-SW sample stream

9.0 Surface Water: *In Situ* Large Volume Water Sampler

9.1 Introduction

We have chosen to include the measurement of semi-volatile organic compounds (SOCs) in lake water because it is a direct link to the atmosphere during snow- and ice-free periods of the year. The current-use pesticides that are included as target analytes may only be detectable in the ecosystem during periods of use (Spring – Fall) and these use periods may not overlap with the period of snowfall and snow sample collection. Although some of the current-use pesticides may not bioaccumulate in fish (and may not be detectable in fish tissue) they may have other adverse affects on aquatic ecosystems. For these reasons, we believe it is important to measure SOCs in lake water at the WACAP sites during late Summer or early Fall.

Water will be sampled *in situ* from all WACAP lakes at the same time that fish are sampled during the ice-free summer season on the schedule of 4 sites per year (6 sites in the third year). Final procedures will be developed during early 2003 and field-tested prior to adoption by WACAP investigators. At the present time, we plan to filter and extract 50 L of water per sample *in situ* and are investigating the use of various sorbants, including XAD-2 resin and the modified divinylbenzene sorbants that will be used to extract snow samples. Lake water will be filtered to remove suspended particulate matter and the filter removed from the system, along with the sorbant column, and extracted and analyzed. Each 50 L sample is expected to take 4-6 hours to collect and extract with the Infiltrex System.

9.2 Sample Collection

The Infiltrex Pumping System (Axys, Vancouver, B.C.) contains a filter for trapping suspended particulate, followed by an extraction column packed with sorbants for trapping dissolved analytes. This system has traditionally been used with XAD-2 resin as the sorbant. Because XAD-2 is not an ideal resin for all of our analytes, and because we would like to make a direct comparison to the concentration of SOCs in the snow samples, the goal of the analytical method used to extract lake water samples is to quantitatively extract 50 L using the same sorbant that is used to extract the snow samples. We have been able to purchase the same hydrophilic and hydrophobic divinylbenzene phases, in bulk, from Baker and will pack the columns used in the Infiltrex system with these materials instead of XAD-2 resin. We are currently determining the mass of these resins required to trap the analytes from 50 L of water and will compare these results to the use of XAD-2 resin. The column will be packed with an initial layer of sorbant, followed by a back-up layer of sorbant to determine if there is analyte break-through during the *in situ* extraction. Recovery experiments are being conducted in the PI's laboratory with the Infiltrex System and the first field deployment and validation took place in early October 2002.

Duplicate samples will be taken (i.e. two separate system runs with a new filter and sorbant column) from both the epilimnion and hypolimnion of lakes that are thermally stratified by a temperature differential equal to or greater than 4° C. The strength of temperature stratification will be determined with a portable field themistor. The sampler will be deployed in the middle of each stratified lake layer. In the case that the lake is not stratified, duplicate

samples will only be collected from the middle of the water column. All sampling will be performed over the deepest portion of the lake.

Filters and sorbant columns will be prepared in the laboratory and appropriately sealed to prevent contamination during transport to the field sites. At the field site, new filters and sorbant columns will be installed and the submersible pump will be programmed for the attributes desired for the run (i.e. start time, flow rate, ending criteria, etc.) using hand-held, programmable, portable, battery operated computers. When the run is finished, the sampling parameters will be verified and recorded using the computer.

9.3 Sample Transport and Storage

The filter and the sorbant columns will be removed from the pump after the run time is finished, labeled, sealed to prevent contamination. The filter and column will be stored in coolers with ice packs, and shipped via overnight courier to the SEC Laboratory, where they will be stored in the freezer until extracted.

9.4 Sample Preparation and Analysis

The concentration of SOCs in the particulate and dissolved phases in lake water will be determined separately. The filters and sorbant will be extracted using an Accelerated Solvent Extraction (ASE) System in the SEC laboratory and the extract analyzed for the target analytes (see Table 3.1.2).

ASE is a relatively new extraction technique used for extracting SOCs from solid environmental matrices such as fish, sediment, and vegetation. This technology replaces traditional Soxhlet extraction and uses much smaller volumes of organic solvents, at elevated temperatures and pressures, and significantly less time than historical extraction techniques. A Dionex ASE 300 system is located in the OSU laboratory and the PI has experience with the use of this instrument for the extraction of SOC from solid environmental matrices (Simonich et al., 2000). The ASE System will also be used to extract the analytes off of the sorbants that are used in the extraction column and sodium sulfate will be used to remove excess water from the extracts. The PI's laboratory has developed a method for extracting atmospheric particulate from glass fiber filters using the ASE system and this method will be modified for the extraction of lake particulates from filters.

9.5 Quality Control

Standard laboratory procedures will be followed for QA/QC involving development of standard curves, duplicate and blank analysis. The specific frequency and numbers of these QA samples will be determined during the final phases of the methods development phase. Lake water field blanks will consist of bringing extra sorbant packed columns and filters into the field, installing the column and filter into the Infiltrex System, deploying the system without collecting a water sample, and removing the column in the same way that it is done for a real sample. The sorbant column and filter will be returned to the laboratory, extracted, and analyzed and used as a field blank.

10.0 Sediment

10.1 Introduction

The objective of the sediment work is to develop decennial to century trends in contaminant (SOCs and metals) flux to the 14 WACAP catchments by dating and analyzing sediment cores from each lake. The sediment analysis and interpretation will be the primary way in which longer term trends will be evaluated and quantified for each catchment. Patterns of contaminant loading in individual catchments will be used to infer processes of atmospheric transport and catchment deposition.

10.2 Sample Collection

Sediment cores will be obtained from each lake during the year in which the catchment in that park is studied intensively. We will core in the summer, using a floating platform made from the inflatable cataraft. The coring locations in each lake will be selected before visiting the lake by examining bathymetric maps of the lakes. Cores will be taken from deep water (i.e. profundal) sites that have a relatively uniform depth and that are located distant from steep sided features that could contribute catastrophic or irregular sedimentation rates due to slumping or sediment focusing. Site locations will be determined using GPS and stored as electronic waypoints in addition to being recorded in field notebooks.

A UWITEC gravity corer with an 86 mm internal diameter will be used to collect at least two sediment cores from each lake. Our target is to obtain cores between 25 and 50 cm in depth. A winch fitted with a depth counter and stainless steel aircraft cable will be used to deploy the coring device. The depth of penetration of the coring device in the sediments is controlled by the amount of external weight added to the device. The amount of weight required is determined by trial and error at each lake.

The sediment coring device can be configured for use in three retrieval modes. The core can be held by the surface tension with the side of the core tube and by a “flapper” device on the top of the core that seals the tube when it is retrieved through the water column. There are also two closing devices that can be fitted to the distal end of the corer. One is an elastic ball closure and the other is a hydraulically operated tube closure. These can be used if the sediments are of a *dy* consistency (unconsolidated gelatinous sediments) that does not adhere well to the sediment core tubes.

Intact cores will be examined to determine that the surface layer is intact and that the core was taken in a vertical plane. If acceptable, they will be capped and put in a rack for transport to a location where core sectioning will be accomplished. Cores will be sectioned at lakeside the same day as collected at lakes that we have accessed with pack animals; cores from the Alaska lakes that are accessed by aircraft may be sectioned after being flown back to the National Park headquarters. Sectioning involves extruding and precisely slicing the core in 0.5 cm or 1.0 cm increments with stainless steel implements. Cores will be sectioned in 0.5 cm increments for the first 10 cm of the core, and then in 1.0 cm increments for the remainder of the core. The first 37 intervals, to 27 cm, will be placed in a pre-cleaned 250 ml wide-mouth glass jar with a cleaned

aluminum foil cap liner, labeled with lake name, core number, and interval. Intervals below 27 cm will be placed in 24 oz. Whirl-Pak bags.

10.3 Sample Transport and Storage

Each core will be sectioned into a total of 36 glass jars and Whirl-Pak bags. Each jar will be placed in a bubble-wrap pouch and then stored in a tray in a cooler for transport from the lake site. Whirl-Pak bags will be included in the same cooler, so each cooler will contain one core. The coolers will be shipped via overnight courier to the WRS Analytical Laboratory, where they will be stored in the refrigerator until processed.

10.4 Sample Preparation and Analysis

The first step in processing sediment cores is to ensure that the stratigraphy of the core is intact (i.e., the layers of sediment were deposited in chronological order and have not been disturbed) by determining the date of sediment layers within the core. The most widely accepted dating technique used to develop chronologies for lake sediments deposited over the last 200 years is one involving the natural radioactive isotope of lead, ^{210}Pb (half-life of 22.3 y). This method has been used very reliably where the sedimentation rates are relatively constant and the sediment stratigraphy is unambiguous. ^{210}Pb occurs naturally as one of the products of the ^{238}U decay series (Appleby, 2001). Other radioisotopes used to date sediment cores are ^{137}Cs and ^{241}Am, and all three isotopes use a non-destructive method by counting gamma ray emissions (Appleby et al., 1986; Appleby et al., 1991). Ten to twelve sections from a core will be used to determine dates. If the dating sequence is acceptable as determined by adequate fit of the Constant Rate of Supply (CRS) (Robbins, 1978) or Constant Initial Concentration (CIC) model, we will proceed with other physical and chemical analyses.

Each section from a core will be homogenized and subsampled initially into two aliquots for the following analyses:

1) SOC analyses: Wet sediment will be stored in the original glass jars and frozen until extracted for SOC analyses;

2) Sediment for freeze-drying for dating, spherical carbonaceous particle (SCP), metals, Hg, and total organic carbon analyses. Sediment will be freeze-dried for at least 24 hours.

Figure 10.1 shows the sediment sample flow diagram and the analyses that will be performed in sequence. A one-gram aliquot of the dried, ground sediment will be shipped to a laboratory for dating. No additional analyses will proceed until after the dating results indicates that the core stratigraphy is intact and can be interpreted unambiguously.

SOC Analyses (wet sediment)

The sediment sections will be thawed, mixed with sodium sulfate and extracted using ASE. ASE has been previously used to extract SOCs from sediment and soil

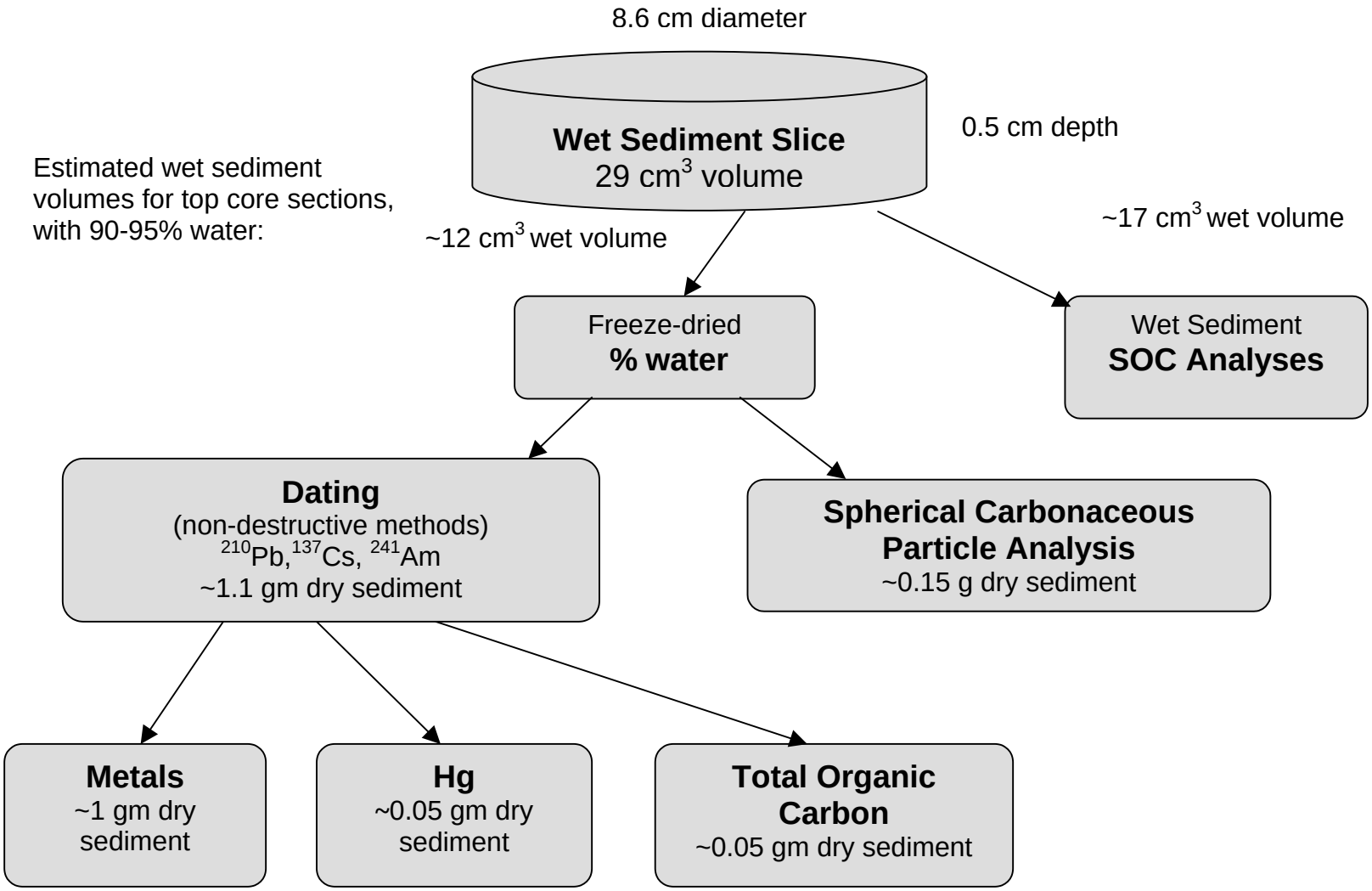


Figure 10.1 Sediment sample flow diagram

(Zhu et al., 2000; Martens et al., 2002). Extract purification will include silica or alumina column chromatography. Method development for the sediment samples began in late Fall 2002.

Physical/Chemical Analyses (dried sediment)

1) Percent moisture: water content will be determined by weighing the wet sediment, freeze drying, and then weighing the dry sediment at the WRS Analytical Laboratory
2) SCP analyses: Approximately 0.15 gram of dry sediment will be removed from the freeze-dried portion before the sediment is ground, and shipped to:

   Dr. Neil Rose
   Environmental Change Research Centre
   University College London
   26 Bedford Way,
   London, UK WC1H 0AP

3) The remaining dry sediment will be ground by hand using an agate mortar and pestle.
4) Transfer approximately 1 gm of dried, ground sediment to a plastic vial to send to the dating laboratory. If sediment used for dating also needs to be used for other analyses (usually in the top intervals with high water content), then the sediment is transferred into small Teflon vials that can be sealed. This sediment is not handled during the dating process. Ship the sediment for dating to:

   Dr. Peter Appleby
   Liverpool University Environmental Radioactivity Research Centre
   University of Liverpool
   Liverpool, UK L69 3BX

5) Metals analyses: Approximately 1 gram of dry sediment will be shipped to the USGS Boulder Laboratory for digestion and metals analyses.
6) Hg analyses: Approximately 0.05 gram of dry sediment will be used for Hg analysis at the WRS Analytical Laboratory.
7) Total organic carbon: Approximately 0.05 gram of dry sediment will be analyzed for total organic carbon at the WRS Analytical Laboratory.

10.5 Quality Control

Information regarding core length, color and physical appearance with depth will be recorded on prepared data sheets prior to sectioning along with the details of the coring site. In addition, a digital image of each core surface and vertical condition will be made through the Plexiglas core tube. Labels will be permanently fixed to all containers of sliced sediment and filled out in permanent marker. All original data sheets will be carried as personal baggage during transit and photo copied and kept in separate locations as soon as facilities permit.

11.0 SOC Analyses

All SOC analyses will be conducted at the Simonich Environmental Chemistry (SEC) Laboratory, 1161 Agricultural and Life Sciences, Oregon State University (OSU), Corvallis, Oregon.

11.1 Laboratory Organization and Responsibilities

The SEC Laboratory is a research laboratory in the Department of Environmental and Molecular Toxicology and the Department of Chemistry at OSU. This laboratory is responsible for developing and validating methods for extraction and SOC analyses in all WACAP sample matrices, including snow, lake water, fish, sediment, vegetation, and non-fish subsistence native food, and will analyse all WACAP samples for SOC analysis. The laboratory uses gas chromatographic mass spectrometry (GS/MS) with both electron impact (EI) ionization and negative chemical ionization (NCI).

The laboratory is directed by the principal investigator, Staci Simonich. Following are the personnel in the research team with their primary responsibilities:

Glenn Wilson: Faculty Research Assistant; analytical method development and validation, field sampling and sample processing

Dave Schmedding: Faculty Research Assistant; analytical method development and validation, field sampling and sample processing

Kimberly Hageman: OSU Post-Doctoral Associate; analytical method development and validation, field sampling and sample processing

Sascha Usenko: OSU Ph.D. student in Department of Chemistry; method development for snow and lake water, field sampling and sample processing

Luke Ackerman: OSU Ph.D. student in Department of Chemistry; method development for fish, field sampling and sample processing

Eli Moore: OSU undergraduate student in Department of Chemistry and Bioresources Research; method development for vegetation, field sampling and sample processing

Judy Wang: OSU M.S. student in Department of Chemistry; method development for sediment, field sampling and sample processing

Lisa Deskin: OSU undergraduate student in Department of Chemistry and Bioresources Research; method development for vegetation, field sampling and sample processing

11.2 Target Analytes

Significant consideration has gone into the selection of target analytes for WACAP. The target SOCs and stable isotope labeled surrogates and internal standards for this project are given in Table 11.2.

Table 11.2 WACAP target SOCs, surrogates, and internal standards

Electron Impact Ionization	Negative Chemical Ionization
PAHs: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene Pesticides and degradation products: o,p'-DDT*, p,p'-DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon, Demeton S, Ethion, Etradiazole, Malathion*, Parathion and Methyl - Parathion, Phorate, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine Surrogates: d_{10}-Fluorene, d_{10}-Phenanthrene, d_{10}-Pyrene, d_{12}-Triphenylene, d_{12}-Benzo[a]pyrene, d_{12}-Benzo[ghi]perylene, d_{14}-EPTC, d_{10}-Phorate, d_5-Atrazine, d_{10}-Diazinon, d_7-Malathion, d_{10}-Parathion, d_8-p,p'-DDE, d_8-p,p'-DDT, d_6-Methyl Parathion, d_{13}-Alachlor, d_{11}-Acetochlor Internal Standards: d_{10}-Acenaphthene, d_{10}-Fluoranthene, d_{12}-Benzo[k]fluoranthene	PCBs: PCB 52 (2,2',5,5'-Tetrachlorobiphenyl), PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl) Pesticides and degradation products: Hexachlorocyclohexanes (HCH) - α*, β, γ-(lindane), and δ, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlor Epoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex Polybrominated Diphenyl Ethers Surrogates: $^{13}C_{12}$ PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), $^{13}C_{12}$ PCB 180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl), d_{10} - Chlorpyrifos, $^{13}C_6$-HCB, d_6-γ-HCH, d_4-Endosulfan I, d_4-Endosulfan II Internal Standards: d_{14}-Trifluralin

PAHs have been chosen as target analytes because they overlap (in part) with the European Mountain Lake Ecosystems: Regionalisation, Diagnostic, and Socio-Economic Evaluation (EMERGE) program and they are the only SOCs included in the target analyte list that are produced by combustion sources. To date, the majority of air measurements of trans-Pacific transport have been for combustion derived pollutants such as CO, NO_x, and O_3. PAH measurements will help link this study to these atmospheric measurements. In addition, it is possible that the PAH distribution in snow could be used to distinguish between fossil fuel and biomass combustion source emissions.

It is possible that, if helicopters are used to access sampling sites, matrices that are exposed to the atmosphere (snow, lake water, vegetation) may be contaminated due to helicopter emissions because PAHs are produced from combustion sources. If a helicopter is used to access a sampling site and these matrices show unusually high levels of PAHs, compared to sites that were not accessed by helicopter, these PAH measurements will be discounted.

Selected polychlorinated biphenyl (PCB) congeners have been chosen as target analytes (see Table 12.2.). The presence of PCBs will be indicative of emissions from industrial and urban North American and Asian sources. These congeners overlap, in large part, with the EMERGE project and current and previous work by Canadian researchers. Because of the limited budget, we have chosen not to measure all 209 PCB congeners but instead to analyze for two ecologically relevant congeners within each chlorination level that responds well by electron capture negative ionization (ECNI) mass spectrometry (tetra- to heptachlorobiphenyls). By analyzing for PCBs with a relatively wide range of chlorination levels, we will likely see evidence of cold condensation as a function of vapor pressure, within a single class of compounds.

The target analyte list also includes persistent organochlorine pesticides such as DDT, hexachlorocyclohexanes, chlordanes, endosulfans, dieldrin, and hexachlorobenzene and some of their degradation products. These pesticides are included as target analytes to estimate emissions from Eurasia and North American agricultural sources. In general, these same organochlorine compounds have been measured in previous and current studies in the field of atmospheric deposition to high elevation ecosystems (see Table 2.1.1). If detected, certain organochlorine pesticides (like DDT) may serve as tracers for current-use of these pesticides in Eurasia.

Finally, we have chosen some of the North American current-use pesticides, including organophosphorus, triazine and carbamate pesticides, as target analytes because they may serve as tracers for North American air emissions and may be transported and deposited to high elevations during periods of use (Spring-Fall). Because these compounds are not as persistent in the atmosphere or in environmental matrices as many of the other target compounds, we have included some of their degradation products as target analytes. Upon volatilization into the atmosphere, the parent pesticide may undergo atmospheric transport and transformation to a degradation product that is then deposited to high elevation ecosystems. We believe the study of current-use pesticides in high elevation ecosystems will be challenging, but their inclusion is fairly novel and may help us understand the potential impact of current-use pesticides on these ecosystems.

11.3 Method Validation

New analytical methods are being developed and validated to measure the wide range and number of target SOCs for WACAP. The order of priority for method development by sample matrix is snow, lake water, fish, vegetation, sediment, and moose meat. Additional assessments for precision, accuracy, and detection limits are performed during method validation, including the following:

- Precision will be assessed from the analysis of replicate laboratory samples in the actual sample matrix. If the RPD > 50% for the replicate laboratory samples, the method will either be improved before sample analysis, or the analyte will be dropped. The data from the replicate laboratory samples will be reported in the SOPs for SOC analysis of each matrix.
- Accuracy will be assessed from the %recovery of target analytes (see Table 2.1.1) over the entire method. Any target analyte that is not recovered at 30 to 130% of its spiked value in the matrix will be flagged. The results from these matrix spike samples will be reported in the SOPs for each matrix.
- Sample-specific estimated detection limits (EDLs) will be calculated using the approach described in EPA Method 8280A, "The Analysis of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)." For each matrix, EDLs will be determined for one sample per park per year. The EDL is an estimate of the concentration of a given target analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The estimate is sample-specific as well as analysis-specific (i.e. the EDL may vary with sample size, dilution factor, etc.). The following equation is used to calculate the EDL:

$$EDL = \frac{2.5 \times C_{is} \times H_n \times D}{H_{is} \times RF}$$

where:

C_{is} = The concentration of the internal standard in the sample.

H_n = The peak height of the noise for the quantitation ion at the target analyte's retention time if the target analyte is absent from the sample or near the target analyte's retention time if the target analyte is present in the sample.

D = The dilution factor, or the final volume of the sample divided by the initial volume.

H_{is} = The peak height of the internal standard.

RF = The response factor, or the ratio of the area of the target analyte to the that of the internal standard multiplied by the ratio of the concentration of the internal standard to that of the target analyte. Because RF can vary with concentration, the RF used in this equation is that determined from the lowest concentration calibration standard in which the target analyte is still detected. Thus, the calibration standard used to determine the RF will vary with specific target analyte.

When it is feasible, method detection limits (MDLs) will also be calculated for matrix samples using the approach described in CFR 136 Appendix B, Revision 1.11 with the following equation:

$$MDL = t_{(n-1,\ 1-\alpha=0..99)}\ (S)$$

Where: $t_{(n-1,\ 1-\alpha=0..99)}$ = the Student's *t*-value appropriate for a 99% confidence level with n-1 degrees of freedom and *S* = the standard deviation of the replicate analysis.

It will not be feasible to calculate MDLs for cases in which the analytical method requires large quantities of matrix, where the matrix is difficult and/or costly to obtain, and/or where the sample preparation method is particularly time-consuming. For example, the method for analyzing snow requires 50 kg of snow per sample and a number of time-consuming preparation steps including (a) melting the snow without heat for ~24 hours, (b) extracting analytes from snow using solid-phase extraction (6 hours per sample), (c) performing sample clean-up with gel permeation chromatography, (d) performing sample clean-up with silica gel chromatography, and (e) performing solvent exchange and sample volume reduction between steps. Also note that the SOC analyte list includes 86 different chemicals with MDLs expected to vary by up to two orders of magnitude. Since the procedure for determining MDLs requires that the entire analytical procedure be conducted (a) several times to determine the correct concentration for spiking and then (b) an additional seven times to determine the MDL, it would, for example, be beyond the scope and budget of this project to determine MDLs in snow.

11.4 Standard Operating Procedures

SOPs are prepared and followed in the SEC Laboratory. Appendix A contains the following SOPS that will be followed for WACAP research:

Glassware Cleaning
Preparation of Primary Analytical Standards
Cleaning and Packaging Teflon Bags for Snow Sampling
Use of the Accelerated Solvent Extractor
Use of the TurboVap Concentration Workstation
Measurement of Semi-Volatile Organic Compounds in Snow Samples

Measurement of Semi-Volatile Organic Compounds in Lake Water
GC/MS EI Sample Analysis
GC/MS NCI Sample Analysis

New SOPs are developed as new instrumentation and/or procedures become available. The following SOPs are in preparation:

Sampling Lake Water for Semi-Volatile Organic Compounds
Extraction and Filtering of High Elevation Lake Water Samples via the Infiltrex 100
Use of Gel Permeation Chromatography Sample Cleanup System
Measurement of Semi-Volatile Organic Compounds in Sediment
Measurement of Semi-Volatile Organic Compounds in Fish and Subsistence Foods
Measurement of Semi-Volatile Organic Compounds in Vegetation

11.5 Quality Control Procedures

Quality control procedures are used in the laboratory to monitor analytical instrument performance and provide feedback so corrective actions can be taken if necessary. Error in measured SOC concentrations can arise from inadequate instrument calibration, sample contamination, and/or analyte loss during sample preparation. The SEC Laboratory analyzes samples to estimate precision, accuracy, contamination, and to monitor completeness, calibration, and detectability. These samples are described below and summarized in Table 11.5.1.

Precision

Quantitative measurements of precision will include co-located field duplicate samples and replicate instrument injections. Field duplicates will represent approximately 10% of the total collected field samples, and replicate instrument injections will represent a minimum of 10% of the extracts injected for analysis. Acceptance criteria (see Table 11.5.1) for SOCs measured in replicate field samples, laboratory samples, and instrument injections will be based on total PCBs and individual pesticides and PAHs.

The overall variance of the measurements will involve pooled data from co-located field duplicates. Since these field duplicates are routine samples in which the actual concentration is unknown, the estimate of overall variance may be influenced by concentration and matrix background. Field duplicate samples contain a component of spatial uncertainty that cannot be separated from the measurement uncertainty. However, if the replicate laboratory precision estimate is deducted from the field replicate precision estimate, an estimate of the field sampling uncertainty can be obtained.

Accuracy

Accuracy will be assessed from the recoveries of isotopically labeled surrogates spiked into individual field samples, and from the analysis of SRMs. Loss of target analytes is expected during sample preparation since the methods for analyzing SOCs involve complex sample

Table 11.5.1 Quality Control Samples and Objectives for SOC Analyses

QA Criteria	QC Code	Sample Type	Frequency	Required Objective	Control Action
precision	FP	field; replicate samples	10 %	total PCBs, each pesticide and PAH, RPD <100%	re-analyze if sample available; otherwise flag samples FFP
	IP	instrument; replicate injections	10 %	total PCBs, each pesticide and PAH, RPD <25%	re-analyze same or alternate sample; otherwise flag samples FIP
	LP	laboratory; replicate analyses of matrix spikes	method validation	total PCBs, each pesticide and PAH, RPD <50%	investigate source of imprecision
accuracy	SR	surrogate spikes	all samples	30% < Recovery < 130%	investigate sources of loss
	AR	matrix spikes	method validation	30% < Recovery < 130%	investigate sources of loss
	RM	standard reference material	10% for relevant matrices	within vendor acceptance window	reanalyze SRM and/or determine source of discrepancy
contamination	FB	field blank	10%	< 20% of associated sample mass	flag samples FFB; find source of contamination
	LB	lab blank	5%	< 5% of associated sample mass	run 2nd LB; eliminate source of imprecision; flag sample FLB
completeness		field samples		90%	no action; % reported
calibration	IC	instrument multiple point calibration - 4 point	monthly	$r^2 > 0.95$	reoptimize instrument, repeat calibration
	PS	instrument performance std	1/batch	± 30% of actual mass	rerun calibration curve
detectability	DL	MDL study	1/project		reported in yearly QA Report
	RFS	routine field samples	all samples	> MDL	flag BDL

preparation schemes. However, by using carefully selected surrogates to quantify loss, errors in accuracy are expected to be minimal even when target analyte loss occurs. Twenty-four different stable isotope labeled surrogates will be injected into each sample at the beginning of the sample preparation procedure. Each target analyte will then be quantified against the stable isotope labeled surrogate that is expected to behave most similarly to it during sample preparation and analysis. If the recovery of stable isotope labeled surrogates does not fall within 30 and 130%, the sample will be flagged and the source of loss or quantification error will be investigated.

When possible, SOC methods will also be evaluated by using them to analyze SRMs from NIST. SRMs are currently available for New York/New Jersey Waterway Sediment, Lake Superior Fish, Organics in Cod Liver Oil (see section 2.1). If the measured concentration values are not within the vendors' acceptance windows, the cause of error will be determined before proceeding with the analysis of that matrix.

Contamination

Potential sample contamination will be monitored by analyzing field blanks (10% of samples) and lab blanks (5% of samples). If field blanks contain greater than 20% of the mass in associated samples, or if lab blanks contain greater that 5% of the mass in associated samples, the samples will be flagged and the source of contamination will be identified.

See section 3.4 for a description of the strategy used to collect field blanks. Field blanks for lake water sampling will consist of bringing extra Speedisks and glass fiber filters into the field, installing the Speedisk and glass fiber filter into the Infiltrex System, and then removing the Speedisk and glass fiber filter in the same way that it is done for an actual sample. The Speedisk and glass fiber filter will be returned to the laboratory, extracted, analyzed, and used as a field blank. Field blanks for snow sampling will be collected by rinsing the snow-sampling equipment with organic-free water in the field, collecting the rinsate in a Teflon bag, and then treating the rinsate identically to snow samples. The SOPs for snow sampling and lake water sampling in Appendix A provide more information. Field blanks for fish, vegetation, sediment, and moose samples will consist of the storage container being taken to the field and returned to the laboratory, extracted and analyzed.

Laboratory blanks will consist of all of the sample manipulation procedures required to analyze a given matrix, however the matrix will not be present. Laboratory blanks will be used to monitor the degree of background contamination introduced during the laboratory analysis. The laboratory blank concentrations will be subtracted from the measured field sample and field blank concentrations.

Completeness

Completeness is the measure of the number of valid samples (meeting all QA requirements) obtained compared to the number required to meet the objectives of the study. Overall completeness is the number of valid samples compared to the number planned. Laboratory completeness is the number of valid samples obtained compared to the number analyzed. Both types of completeness will be reported for the WACAP project. The acceptance

criteria for completeness is 90%. The projected number of field samples and sampling locations are shown in Table 11.5.2.

GC/MS Calibration

All samples will be analyzed for the target analytes given in Table 11.2, provided that the analytical method for a given matrix has been validated for the target analytes and meets the data quality objectives outlined in Table 11.5.1. Two gas chromatographic mass spectrometers (Agilent 5973) will be used for the analyses and the target analytes will be quantified using selected ion monitoring. One GC/MS will be operated in EI ionization mode, while the other GC/MS will be operated in NCI mode (see Table 11.2 and the corresponding SOPs in Appendix A). To minimize instrument-associated errors, calibration standards will be run at least once per month and calibration curves will contain a minimum of 4 points and must have an $r^2 > 0.95$ (see Table 11.5.1). Instrument performance standards will be analyzed with every batch of samples. If the concentrations of target analytes measured in performance standards do not fall within ± 30% of actual concentrations, calibration standards will be rerun or the source of error will be addressed.

Table 11.5.2 Projected number of WACAP Field Samples

Sample Matrix	Assumptions Made	2003 Sequoia and Rocky Mt.	2004 Noatak and Denali	2005 Olympic, Mt. Rainier, and Glacier
Snow	14-19 sites/year, 3 reps/year, 3 blanks/year	20	23	22
Lake Water	1 rep/park, 2 sites/park, 2 analyses/sample (filter and sorbant)	12	12	18
Lake Sediment	1 core/site, 8 sections/core	32	32	48
Fish	10 fish/site	40	40	60
Lichen	15 samples/park	30	30	45
Willow Bark	15 samples/park	30	30	45
Moose	21 samples total		11	10
Total Number of Samples		164	178	248

Detectability

Detectability is a measure of the degree to which an analysis can reliably establish an unknown's value as greater than zero. If regular samples are below the method detection limit for a target analyte (see sections 2.1 and 11.3), they will be flagged BDL in the data base for below detection limit.

Representativeness

This expresses the degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness with respect to the field sampling is a measure of the parameter variation at a sampling point and is evaluated by collecting random duplicate samples.

Comparability

Comparability addresses the confidence with which one data set can be compared to another. The comparability of one year's data with another is maintained by adherence to standard operating procedures. Any changes to sampling or analytical procedures are thoroughly evaluated and documented. Comparability between laboratories and projects will be assessed through the analysis of Standard Reference Materials.

11.6 Sample Storage

All WACAP samples received by the Simonich Lab will be stored in the walk-in freezer 1124C located on the first floor of the Agricultural and Life Sciences Building on the Oregon State University Campus. This freezer is maintained at -20º ± 5ºC and is monitored via an external dial thermometer located on the outside wall of the freezer and the temperatures are recorded on a log sheet on the wall immediately outside cold room 1124B. The temperature is also monitored via a max-min thermometer that is maintained on a shelf inside the freezer and recorded a minimum of three times per week on the log sheet. As an additional record, a Vemco remote temperature logger is located inside the cooler and is programmed to record temperatures once every 30 minutes. This logger has a range of -30ºC to +40ºC, and a resolution of 0.3ºC and an accuracy of 0.5ºC. Since the logger can store 16,000 measurements, the current plan is to download and plot the data if the other measurements suggest a problem or on an annual basis under normal operation to provide a contiguous annual record of the cooler's performance. If the temperature is observed outside the acceptable limits, the laboratory principal investigator is notified to begin corrective action and the freezer contents will be moved to a nearby backup freezer unit (1112B) until the problem has been corrected.

12.0 Mercury and Metals Analysis

Mercury analyses for snow samples will be conducted at the USGS Wisconsin Mercury Laboratory. All other mercury analyses will be conducted at the WRS Analytical laboratory. All metals analyses will be conducted at the USGS National Research Program (NRP) Laboratory in Boulder, CO. The QA Project Plan for the USGS NRP Laboratory is included as Appendix B. The QA Plan for the WRS Analytical Laboratory is attached as a separate document.

C. DATA

13.0 Data Management

13.1 Introduction

WACAP data will be reported in Microsoft Excel, and will be developed into a Microsoft Access database. Excel is used by most laboratories, and can be imported into many statistical software programs. Excel files will be structured similar to database files so they can be easily imported into Access, with columns becoming fields, and rows becoming records. Each sample type (e.g., snow, fish, water, sediment, lichen, bark) will have a separate Excel file.

13.2 Database

WACAP will have 14 sites, plus some Parks will have additional snow sampling sites. Each site will have snow analyses each year, and then will have data from one year from the different matrices, such as fish, water, sediment, lichen, bark, and for the Alaska Parks, subsistence foods. Each sample matrix will also have multiple analyses (SOCs, mercury, etc.) performed by different laboratories. There will also be field observations and ancillary data (e.g., bathymetric maps) that will be kept for reference. We will want the data in a format that we can:

- combine all data from the same matrix into one file
- sort the data by site
- sort the data by matrix
- trace to laboratory QA data
- refer to analytical methods

WACAP sites will be consistent from year to year, so the PARK code and SITENAME will be used to identify each site. The PARK code will be the abbreviations used by the National Park Service, which are created by using the first two letters of the first two words in the park name. Table 13.1 lists the PARK codes for each WACAP Park.

Sample numbers will be assigned based on matrix type according to the sample ID numbers at the WRS Analytical Laboratory. The first digit represents the year, with 3 for the year 2003, 4 for the year 2004, etc. The second digit represents the WACAP project at the WRS Analytical Laboratory and is assigned as “6”. Figure 13.1 lists the sample numbers assigned to each matrix.

Data for each analyte will be stored in three fields that will include the concentration, the analysis date, and the laboratory code as well as the Park code, site name, collection date, and sample number. A numerical code will be assigned to identify each laboratory. QA and method information can then be linked based on the analysis date and laboratory.

Data from each year will be verified and validated at each laboratory, then sent to the PI for that ecosystem indicator and to the data management group in Corvallis. Excel files will be combined into an Access database.

Table 13.1 Park Codes for WACAP Sites

National Park	**Park Code**	**WACAP sites**
Noatak National Preserve	NOAT	Burial
Gates of the Arctic National Park and Preserve	GAAR	Matcharak
Denali National Park	DENA	Wonder
		McLeod or Foraker
Glacier National Park	GLAC	Oldman
		Snyder
Mount Rainier National Park	MORA	Golden
		LP19
Olympic National Park	OLYM	PJ
		Hoh
Rocky Mountain National Park	ROMO	Mills
		Lone Pine
Sequoia National Park	SEKI	Emerald
		Pear

13.3 Distribution

The final database will be in Access, with linked tables containing data for each site and all the ecosystem indicators, and available on CD. Documentation on the CD will include analytical methods, QA plans, and field notes. The data will also be available as Excel files. Our intention is to compile the database with enough information so that the data will be useful in the future.

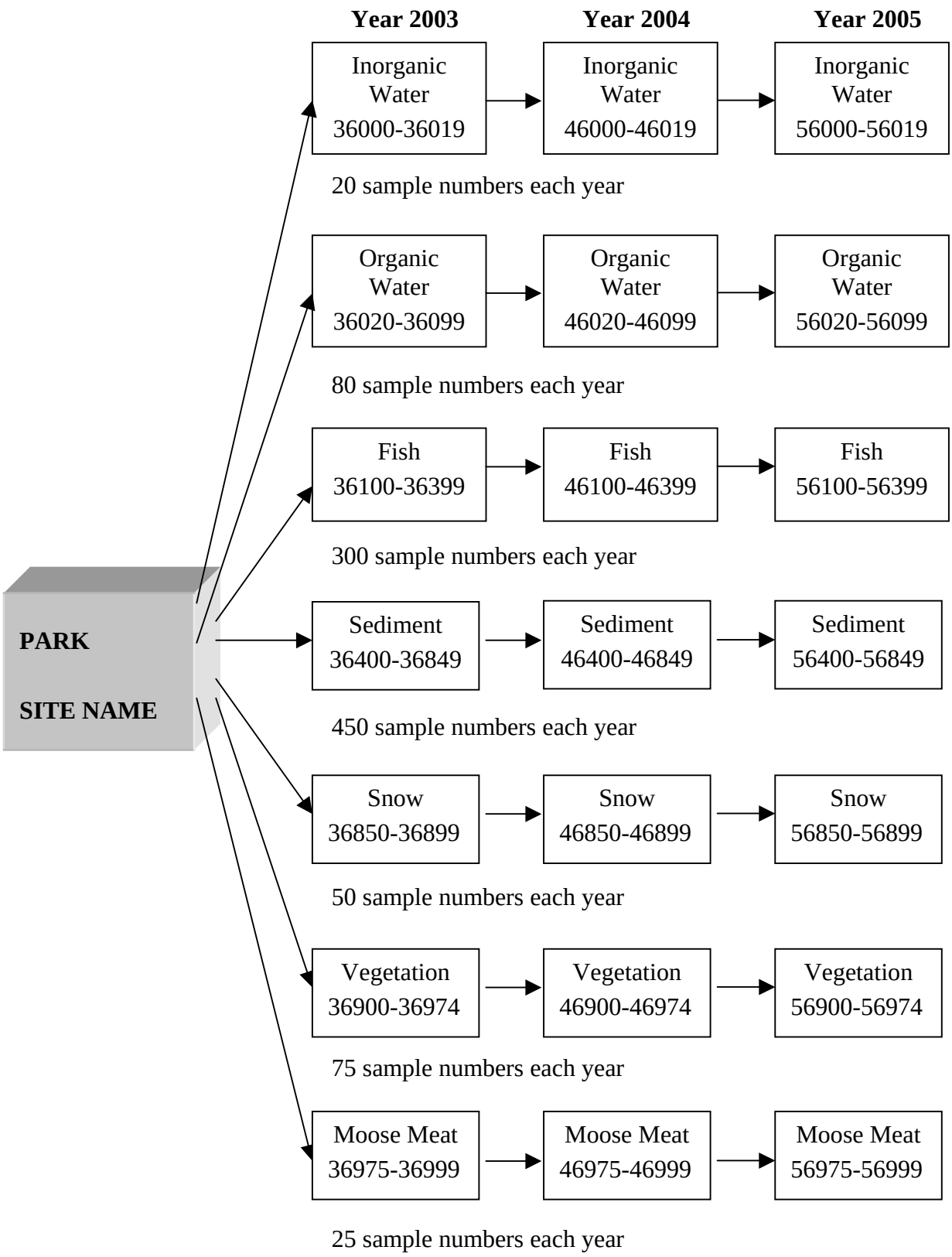


Figure 13.1 Sample Numbers for WACAP Matrices

D. ASSESSMENT/OVERSIGHT

14.0 Performance evaluation

Data comparability issues for WACAP involve both the comparability of data from different laboratories participating in WACAP, and comparing WACAP data with data from other projects. Within WACAP, we have made an effort to have all analyses for each parameter analyzed at the same analytical facility. However, up to six different laboratories will be analyzing WACAP samples (see Table 3.2.1), and even though the samples may be from different sample types (water, fish, lichens, etc.) we still want the analytical results to be comparable. For example, mercury data from fish, sediment, water, and snow will be used to describe the impact of mercury to a catchment. All participating laboratories will participate in external performance evaluation program for analytes when they are available, e.g., major ions, metals, and mercury. Programs for organic compounds are not presently available, so round robin exchanges with other laboratories will be planned. Certified standard reference material will also be used when available.

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Appendix A

Simonich Environmental Chemistry Laboratory

Oregon State University

Standard Operating Procedures

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Staci Simonich
Dave Schmedding
Glenn Wilson
Sascha Usenko
Robert Killin
Susie Genualdi

List of Standard Operating Procedures

Standard Operating Procedure for the Cleaning of Glassware

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Susie Genualdi
February 2003

Standard Operating Procedure for the Cleaning of Glassware

Approvals:

Staci Simonich
Oregon State University
Principal Investigator

Staci L. Simonich 10/7/04
Signature *Date*

Susie Genualdi
Undergraduate Assistant

Susie Genualdi 10/8/04
Signature *Date*

Table of Contents:

1.0 Scope and Application

This method details a procedure to thoroughly clean glassware that is intended for use in qualitative and quantitative analyses.

2.0 Summary of Method

The procedure for cleaning glassware is initialized by a soak in a tub full of hot soapy water. The glassware is then rinsed 3 times with tap water and another 3 times with de-ionized water before being dried in an oven designated for glassware bake out. The oven runs for 12 hours at a temperature of 375^{o}C.

3.0 Definitions

3.1 Micro-90- a suggested concentrated soap used for critical cleaning. Other comparable brands of concentrated soaps may be used instead.

3.2 Tempilstik- a temperature indicator that changes from red to brown after reaching 371^{o}C. Other comparable brands may also be used.

4.0 Interferences

4.1 Work area interference can affect the cleanliness of the glassware. Every effort should be made to avoid cross contamination. This includes soaking the mildly dirty glassware in a separate tub than the heavily dirtied glassware.

4.2 It is also important to keep the clean glassware waiting to go into the oven out of contact with soap, other solvents, and anything that could further contaminate the glassware.

5.0 Safety

5.1 It is important to wear gloves when dealing with the concentrated soap because excessive exposure can be harmful to the health of the individuals subjected to it.

5.2 It is also important to make sure that no flammable solvents have come into contact with the stainless steel tray and the glassware before the tray is placed into the oven.

6.0 Equipment and Supplies

6.1 Nitrile gloves.

6.3 Micro-90 soap.

6.4 Plastic tub (approximately 14L).

6.5 Scrub brushes.

6.6 RO-DI (Reverse osmosis de-ionized) water.

6.7 Stainless steel tray (that can be baked out in an oven at a temperature of 375^{o}C).

6.8 Tempilstik (a temperature indicator stick)

6.9 Forced Air Furnace.

7.0 Quality Control

7.1 It is important to place dirty glassware in tubs full of clean soapy water prior to washing, and avoid placing them in tubs that are already soaking.

7.2 Once the glassware is rinsed thoroughly, there should be no soapy residues. This can be checked by holding the glassware up to the light and looking for rainbow colored films.

7.3 In order to ensure the oven reaches the ideal temperature, a Tempilstik can be used as an indicator. A mark can be made on the stainless steel tray with the Tempilstik, and if the tray reaches above 371^{0}C, the mark will turn from dark red to brown.

8.0 Procedures

8.1 Fill a 14 L washtub ~2/3 full of hot water, and add ~2 capfuls or 30mL of a concentrated soap used for critical cleaning.

8.2 Place glassware in tubs being sure that all open bottles are filled with soapy solution. Allow to sit for ~5 minutes.

8.3 Scrub each piece thoroughly with scrub brushes and rinse off the glassware with 3 rinses of tap water followed by 3 more final rinses of RO-DI water.

8.4 Once the glassware is rinsed thoroughly, place it in a stainless steel tray that can be used for baking.

8.5 Once the tray is full, place it in the Forced Air Furnace at a temperature of 375^{o}C for 12 hours.

9.0 Pollution Prevention

9.1 The chemicals used in this method pose little threat to the environment.

9.2 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

10.0 Waste Management

10.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

10.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington DC, 20036.

Standard Operating Procedure for the Preparation of Primary Analytical Standards for Semi-Volatile Organic Compound Analysis

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Dave Schmedding
March 2003

Standard Operating Procedure for Preparation of Primary Analytical Standards for Semi-Volatile Organic Compound Analysis

Approvals:

Staci Simonich
Oregon State University
Principal Investigator

Staci L. Simonich 10/7/04
Signature *Date*

Dave Schmedding
Senior Research Assistant

Signature 10/11/04
Date

Table of Contents:

1.0 Scope and Application

1.1 This method details the procedure for preparation of primary analytical standards used in the quantitation of semi-volatile organic compounds.

2.0 Summary of Method

2.1 Analytical balance

Due to cost and quantity availability constraints, it is necessary to utilize a five place analytical balance to ensure the accuracy of the weighed out material remains at ±1%. This means the analytical balance used must be capable of weighing 0.01 mg accurately and reproducibly. American Society of Testing Materials (ASTM) class 1 weights must be used to verify the accuracy of the 0.1 mg and 0.01 mg measurements. It is imperative that these weights be handled only with the tweezers provided with the kit to avoid contamination from human contact. The analytical balance must be checked against the ASTM weights biannually or after evidence of the balance being bumped (this will be obvious when trying to zero the balance). The balance must be zeroed at the beginning of each session prior to standards preparation.

2.2 Weighing out materials

Approximately 5 mg of a solid free-flowing neat standard is weighed onto a tared weighing paper and quantitatively transferred to a screw capped vial to which 5 mL of the appropriate solvent is added to make a ~1 mg/mL primary standard. Non free-flowing solids (sticky or hygroscopic material) are weighed directly into the vial after taring the vial. Liquids are transferred via disposable pipet directly into a tared vial. It is not necessary or recommended that exactly 5.0 mg be weighed out, only that the weight be somewhere between 4.5 mg and 5.5 mg.

3.0 Safety

3.1 The laboratory exhaust fume hood should be used when handling solvents.

3.2 Personal Protection Equipment (PPE) should be worn at all times during the procedure. Chemical resistance nitrile gloves should be worn when handling organic solvents. Eye protection should be worn when handling organic solvents and/or operating the manifold under the vacuum.

3.5 Material Safety Data Sheet (MSDS) reports for all solvents should be available in the laboratory.

4.0 Equipment and Supplies

4.1 Analytical balance capable of weighing 1 mg to within ± 0.01mg.

4.2 ASTM Class 1 weight set.

4.3 4 in. x 4 in. glassine weigh paper.

4.4 Modified narrow tip stainless steel spatula.

4.5 7 mL amber vial with Teflon lined screw cap.

4.6 Disposable pipet.

4.7 Waste beaker.

4.8 5 mL Class A transfer pipet.

4.9 Teflon wash bottle with appropriate solvent.

5.0 Procedures

5.1 Solid-free flowing neat materials.

The initial step is to carefully cut standard 4 in. x 4 in. weighing papers into four equal pieces ~ 2 in. x 2 in. This is done to minimize the surface area potentially in contact with the chemical to be weighed. Next a ~ 2 in. x 2 in. square is carefully folded four times from one corner to the other to make it into an open funnel shaped form without touching the inner surface. The paper is then placed on the balance pan and weighed as a tare to five significant places (to the closest 0.01 mg). The material to be weighed must be allowed to warm to room temperature before weighing to avoid condensation which will cause the weight to continually increase as the weighing progresses. The material is transferred from the vial to the lower portion of the weigh paper near the exit point so as to have the smallest practical distance to travel during transfer. After transferring ~ 5 mg of material to the weigh paper, close the door to the balance and allow the balance to stabilize before making the final reading. Co-workers leaning on the bench, open windows, hood drafts, close proximity to refrigerators, freezers, or other laboratory equipment that generates vibrations will likely prevent satisfactory operation of a five place analytical balance. A previously cleaned 7 mL amber screw cap vial fitted with a Teflon liner is opened and placed in close proximity to the balance. With the material on the weigh paper, place the weigh paper into the opening of the vial in a funnel shape and gently tapped on the outside to dislodge the contents. After ensuring a complete transfer, the paper can be reweighed to verify that the transfer was quantitative but this will be

unnecessary after some practice and confidence from repeated reweighing. The next step is to add solvent via a 5 mL Class A transfer pipet. Care should be taken to place the tip against the inside edge of the vial to facilitate consistent tip drainage and ultimate transfer accuracy. It is necessary to use a Class A transfer pipet since it is a ± 0.2% accuracy device which is the same accuracy as the analytical balance when weighing out a 5 mg sample. The final primary standard when properly prepared should then have an accuracy if less than ± 0.5%.

5.2 Non-free flowing solid materials.

Sticky or hygroscopic materials are more difficult to transfer and are handled as in 5.1 above with the exception that the material is directly transferred to the primary standard vial to avoid the loss of material that would have remained on the weigh paper and not be transferred. When dealing with materials that are somewhat hygroscopic, it is necessary to rapidly transfer and note the weight as the material will continually gain weight (especially on days with high humidity) due to condensation. Some experience will be needed to avoid transferring more than ~ 5 mg, since transferring back is both not recommended and generally unsuitable due to the time element and resultant moisture gain.

5.3 Liquid materials.

Materials that are liquid at room temperature are handled as in 5.2 except that a disposable pipet is used to transfer the liquid directly to the primary standard vial. For most organics, a liquid column ~ 1.5 mm. long near the very tip will be close to 5 mg. The liquid should be introduced near the bottom of the vial during transfer to ensure it will be in contact with the 5 mL of added solvent. Often liquid materials will lose weight on exposure to the atmosphere due to volatilization, so some care will need to be taken to minimize the time that both the neat material and the transferred material are exposed to the atmosphere.

5.4 Standards container labeling.

The label prepared for the new primary standards vial should have a unique standards code number from the standards notebook so any questions can be easily referenced to the notebook. The label should also contain the common name of the compound, manufacturer and their product number and lot number, expiration date, concentration, date of preparation, solution solvent, and a mark at the liquid level in the vial after the addition of the 5 mL solvent along with the initials of the individual doing the preparation. All this information should be on a self stick label which is then covered with scotch tape to maintain the integrity of the information in the event of a solvent spill.

6.0 Pollution Prevention

6.1 The Chemicals used in this method have a wide range of toxicity but due to the small quantities handled ever a total spill would pose little threat to the environment or other laboratory personnel.

6.2 For further information on pollution prevention consult, *Less is better: Laboratory Chemical Management for Waste Reduction,* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202)-872-4477

7.0 Waste Management

7.1 The only waste generated will be from rinsing the disposable pipets prior to disposal or from inadvertent spilling during transfer. Both occasions mandate quantitative transfer to the hazardous waste beaker and subsequent proper disposal as covered in the following section.

7.2 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Standard Operating Procedure for Cleaning and Packaging of Teflon Bags For Snow Analysis

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Sascha Usenko
February 2003

Standard Operating Procedure for Cleaning and Packaging of Teflon Bags For Snow Analysis

Approvals:

Staci Simonich
Oregon State University
Principal Investigator

Staci I. Simonich 10/7/04
Signature *Date*

Dave Schmedding
Senior Research Assistant

10/11/04
Signature *Date*

Sascha Usenko
Graduate Research Assistant

Sascha Usenko 10/7/04
Signature *Date*

Table of Contents:

1.0 Scope and Application

1.1 This method details the procedure for cleaning and packaging of teflon bags for snow analysis.

2.0 Summary of Method

2.1 The inner surface of the teflon bags is rinsed twice with solvent, once with ethyl acetate (~45 mL) followed by hexane: acetone 1:1 (~45 mL). Each solvent rinse should last 45 to 60 seconds. Once the teflon bag has been rinsed twice it is allowed to dry. After the teflon bag is dry, fold the opening of the bag in half and then in half again. Cover the opening with one aluminum foil sheet and then fold the bag into a 6" x 6" square. Place the folded bag into two Ziploc® bags (one inside the other) and seal them. These clean and packaged teflon bags are placed in a polyethelene bag (as many needed for one snow sample, usually 2 to 7 bags).

3.0 Safety

3.1 The use of the laboratory exhaust fume hood should be used when handling or in the presence of volatile organic compounds.

3.2 Personal Protection Equipment (PPE) should be worn at all times during the procedure. Chemical resistant gloves should be worn when handling of organic solvents. Eye protection should be worn when handing organic solvents and/or operating the manifold under the vacuum.

3.5 Material Safety Data Sheet (MSDS) reports for all solvents and standards should be available in the laboratory.

4.0 Equipment and Supplies

4.1 Teflon bag

4.2 Ziploc® bags (one gallon size).

4.21 Two Ziploc® bags for each teflon bag.

4.3 Aluminum Foil (~12" x 12" squares, baked at 450° C for 12 hrs).

4.31 One aluminum square for each teflon bag.

4.4 Storage bag (one bag for each snow site).

4.5 Two repipets (50 mL).

4.6 Ethyl Acetate (pesticide grade, ~45mL per teflon bag).

4.7 Hexane: Acetone (1:1, pesticide grade, ~45 mL per teflon bag).

5.0 Procedures

5.1 Take one teflon bag and place ~45 mL of ethyl acetate inside the bag.

5.2 In a laboratory exhaust fume hood, gathering the opening of the teflon bag in one hand (tight enough to prevent leaking).

5.3 Shake the teflon bag and force solvent over the entire inner lining of the bag for 45 to 60 seconds. Ensure that solvent completely rinses the inner lining of the bag.

5.4 Open the bag in the fume hood and release the solvent vapor. Pour the remaining solvent into a waste beaker. Bag does not have to be dry.

5.5 For the second rinse add ~45 mL of hexane: acetone (1:1) to the teflon bag and gathering the opening of the bag again into one hand (remember tight enough to prevent leaking).

5.6 Shake the teflon bag and force solvent over the entire inner lining of the bag for 45 to 60 seconds. Again ensure that solvent completely rinses the inner lining of the bag.

5.7 In the fume hood open the bag and release the solvent vapor. Then pour the remaining solvent into a waste beaker.

5.8 Allow the bag to dry (usually 5 to 10 minutes).

5.9 Once the bag is dry fold the opening in half and then in half again. The folded bag should now be ~6 inches wide at top and bottom and 24 inches long down the side.

5.10 Place the opening of the teflon bag down in the middle of a baked ~12” x 12” square of aluminum foil.

5.11 Fold the aluminum foil square around the opening of the teflon bag to help keep it clean and away from the body of the bag.

5.12 Fold the opening of the teflon bag down the body of the bag three or four times. The bag should be roughly a 6 inch square with the opening covered in foil and wrapped up in the body of the bag.

5.13 Place the folded clean into two Ziploc® bags one inside the other. Each Ziploc® bag should be sealed with as little air as possible to facilitate packing and shipping.

5.14 Open the polyethylene bag and place as many of the clean and packaged teflon bags as needed for one snow sample in the bottom of the bag. One

snow sample maybe collected in 2 to 7 teflon bags (5 to 50 liters per sample).

5.15 After inserting clean and packaged teflon bags in the bottom of the polyethylene bag, wrap the polyethylene bag around the clean and packaged teflon bags.

5.16 Wrap the polyethylene bag up into a bundle (with as little air as possible) and secure it with rubber bands until use.

6.0 Pollution Prevention

6.1 The chemicals used in this method are readily degraded and pose little threat to the environment.

6.2 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction,* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

7.0 Waste Management

7.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

7.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel,* and *Less is Better: Laboratory Chemical Management for Waste Reduction,* both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington DC, 20036.

Standard Operating Procedure

for Use of the Accelerated Solvent Extractor

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Robert Killin
March 2004

How to use the Accelerated Solvent Extractor

By Robert Killin
3/8/04

1) Make sure there is enough N_2 in the tank (which is always on).
2) Check the solvent bottles and make sure they are more than ¼ full (or 500 mL).
    a. Refill by unscrewing the cap and leaving the grey frit on a KimWipe.
3) Get cells, plunger, and funnel from drawers below ASE.
    a. Clean each with solvent (in the order of acetone, DCM, EA, and DCM).
    b. Each cell should be separated (2 caps and center section) and cleaned by themselves.
    c. Recap one end of the cell.
    d. Take a small filter (in drawer) and push it partway down the cell with the plunger.
    e. After ensuring the filter is flat, push it all the way down.
    f. Fill cell with extractable substance. If there is free space, fill with Hydromatrix (in "solid phase solvent" cupboard).
    g. Recap.
4) Press "Trays" button such that the green light is lit on the left.
    a. This means the trays are unlocked and free-rotating.
    b. Do not spin the trays if the green light is lit on the right.
5) Press "Menu" button, then the "4" button on keypad (schedule editor).
6) Set up your schedule, or look for one that matches what extractions you want to do.
    a. Choose a schedule number by looking in the ASE book for unused numbers.
    b. Choose your cell numbers.
    c. Select the extractions you want.
        i. Method 5 is DCM.
        ii. Method 6 is EA.
        iii. Method 7 is Acetone.
    d. Set "rinse" to "ON C" after your last extraction.
    e. Save as the new number (look at ASE book to see open numbers).

7) Press “Menu” button, then the “1” button on keypad (Load method/schedule).
8) Select “schedule” with the “select up” button, then press “right arrow” so you can type your schedule number.
9) With the trays unlocked, spin the cell holder and place the cells.
10) Label the bottles you need and place them into the bottle holder.
    a. Use the clear bottles, not the amber ones.
    b. If you are cleaning, use the blue septa. For extraction of samples, use the Teflon disks.
11) On the keypad, press “Trays” to lock the trays.
12) Press “start”.
13) Monitor 1st extraction to ensure correct pressurization.
14) As soon as extractions are over, press “trays” and remove cells and bottles.
15) Throw away filter and clean cells with solvent before storage.
16) Clean bottles in the usual manner.
17) If there are any problems (i.e. leaks, bad pressurization), press “abort.”

Standard Operating Procedure

for Use of the Turbovap Concentration Workstation

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by
Sascha Usenko
November 2003

How to use the Turbovap Concentration Workstation

By Sascha Usenko
11/20/03

1. Check water level. Fill with DI water if necessary.
2. Activate N_2 (main value only, regulator is preset)
    a. Backpressure should be set at 38-40 psi.
3. Turn on the Turbovap (switch on left side).
4. Press “Select Displayed Condition” until pressure is reached.
    a. Keep the pressure above 3 psi (or Turbovap will beep annoyingly).
    b. Rinse Cell walls during blowdown with solvent.
5. Load sample containers by 1st removing the plastic covers of the positions in use.
6. Close hatch.
7. Press “Endpoint select” until sensor it lit.
8. Press “Start-Stop” for each cell in use.
    a. Keep the pressure above 3 psi (or Turbovap will beep).
9. Rinse Cell walls during blow-down with the appropriate solvent.
10. Wait until Turbovap beeps the finish of a cell.
11. Press “Start-Stop” for the finished cell.
12. Remove sample container and place the plastic cover over the position.
13. Close hatch to continue run.
14. Using a long pipet, rinse the curved area of the cell with the sample.
15. Pipet into a vial.
16. Repeat steps **8-14** for the other samples.
17. When finished, turn off the Turbovap and close the N_2 valve.
18. Leave the hatch open for a few minutes as the water bath cools.
19. Clean cells with soap and water. Bake out 12 hrs at 350°C.

Standard Operating Procedure for the Determination of Semi-Volatile Organic Compounds in Snow Samples

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Sascha Usenko
and Kimberly Hageman
January 2004
Updated June 3, 2004

Standard Operating Procedure for the Determination of Semi-Volatile Organic Compounds in Snow Samples

Approvals:

Staci Simonich
Oregon State University
Principal Investigator

Staci L. Simonich — *Signature* — 10/7/04 — *Date*

Dave Schmedding
Senior Research Assistant

Signature — 10/11/04 — *Date*

Sascha Usenko
Graduate Research Assistant

Sascha Usenko — *Signature* — 10/7/04 — *Date*

Kimberly Hageman
Post-Doctoral Research Assistant

Kimberly J Hageman — *Signature* — 10/11/04 — *Date*

Standard Operating Procedure for the Determination of Semi-Volatile Organic Compounds in Snow Samples

Table of Contents:

1.0 Scope and Application

1.1 This method details the analytical method for the measurement of semi-volatile organic compounds (SOCs) in snow samples.

2.0 Summary of Method

2.1 Snow from a single sample, which is contained in a number of polytetrafluoroethylene (PTFE) bags, is melted without heat in a fume hood. Stable isotope labeled surrogates appropriate to the given sample (see Table 1) are added to each bag. Melted snow is extracted using a combination hydrophilic and hydrophobic divinylbenzene *Speedisk*™. Following the extraction, analytes of interest are eluted from the *Speedisk*™ with appropriate solvents.

2.2 The sample is dried using sodium sulfate to remove water. Once dried, the sample is reduced to ~0.2 mL via nitrogen blow down, exchanged to dichloromethane (DCM), and filtered with a 0.45 µm syringe filter. To remove large diameter molecules that may interfere with target analytes, the sample is subjected to gel permeation chromatography (GPC). The fraction of eluate recovered from the GPC that contains analytes is reduced to ~0.2 mL via nitrogen blow down and exchanged to hexane. To remove polar chemicals that may interfere with target analytes, the sample is introduced to a 20-gram silica solid phase extraction cartridge. The sample is eluted from the column and fractionated using combinations of solvents that range in polarity. Fractions containing analytes are combined and reduced via nitrogen blow down to ~0.2 mL.

2.3 The sample is spiked with stable isotope labeled internal standards (see Table 1). Finally, each sample is analyzed on two different gas chromatographs (GCs) equipped with mass spectrometers (MSs). One MS utilizes electron impact (EI) as the ionization source and the other utilizes negative chemical ionization (NCI).

3.0 Safety

3.1 The laboratory exhaust fume hood is used when handling solvents.

Table 1: Target Compounds, Surrogates and Internal Standards

Electron Impact Ionization	Negative Chemical Ionization
PAHs: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene Pesticides and degradation products: o,p'-DDT*, p,p'-DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon, Demeton S, Ethion, Etradiazole, Malathion*, Parathion and Methyl - Parathion, Phorate, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine Surrogates: d_{10}-Fluorene, d_{10}-Phenanthrene, d_{10}-Pyrene, d_{12}-Triphenylene, d_{12}-Benzo[a]pyrene, d_{12}-Benzo[ghi]perylene, d_{14}-EPTC, d_{10}-Phorate, d_5-Atrazine, d_{10}-Diazinon, d_7-Malathion, d_{10}-Parathion, d_8-p,p'-DDE, d_8-p,p'-DDT, d_6-Methyl Parathion, d_{13}-Alachlor, d_{11}-Acetochlor Internal Standards: d_{10}-Acenaphthene, d_{10}-Fluoranthene, d_{12}-Benzo[k]fluoranthene	PCBs: PCB 52 (2,2',5,5'-Tetrachlorobiphenyl), PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl) Pesticides and degradation products: Hexachlorocyclohexanes (HCH) - α*, β, γ-(lindane), and δ, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlor Epoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex Polybrominated Diphenyl Ethers Surrogates: $^{13}C_{12}$ PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), $^{13}C_{12}$ PCB 180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl), d_{10}-Chlorpyrifos, $^{13}C_6$-HCB, d_6-γ-HCH, d_4-Endosulfan I, d_4-Endosulfan II Internal Standards: d_{14}-Trifluralin

3.2 Personal Protection Equipment (PPE) is worn at all times during the procedure. Chemical resistant nitrile gloves are worn when handling organic solvents. Eye protection is worn when handling organic solvents and operating the vacuum manifold.

3.3 Material Safety Data Sheet (MSDS) reports for all solvents are available in the laboratory.

4.0 Equipment and Supplies

4.1 J.T. Baker *Speedisk*™ Extraction Disk (DVB Hydrophilic)

4.2 J.T. Baker *Speedisk*™ Extraction Disk (DVB Hydrophobic)

4.3 Supelco Visiprep SPE Vacuum Manifold

4.4 *Speedisk*™ Remote Sample Adapter

4.5 Varian Bond Elut® Silica Solid Phase Extraction Cartridge (20 g)

4.6 Support Tubs (10 Liter, one per PTFE bag)

4.7 Syringes (1 mL & 25 µL)

4.8 Lab coat or apron

4.9 Eye protection

4.10 Nitrile gloves

4.11 Laboratory exhaust fume hood

4.11 250 mL amber glass bottles with PTFE resin caps

5.0 Sample Handling and Storage

5.1 Sample transport is documented to establish chain of custody. The EPA office in Corvallis documents the chain of custody between the field site and the EPA office. The Simonich Environmental Chemical Laboratory at Oregon State University documents the chain of custody between the Corvallis EPA office and the Simonich Environmental Chemical Laboratory.

5.2 All snow samples are stored in coolers with blue ice during transport, which is the responsibility of the USGS or USEPA. Snow samples are stored in freezers at -20°C ± 5°C until analysis. Following analysis, samples are stored in a refrigerator at 10°C ± 5°C.

6.0 Procedures

Setup and Preparation of Modified *Speedisk*™

6.1 Remove snow sample from the freezer and place each PTFE bag containing snow in a 10 L support tub. Snow samples are generally divided between six PTFE bags and each bag contains approximately 50 kg of snow.

6.2 Cover each tub with a small black plastic garbage bag and place the tubs in a fume hood. Do not add heat and keep light exposure to a minimum. It will take 18 to 24 hrs for all snow to melt.

6.3 Prepare two modified *Speedisks*™ per sample.

6.3.1 Prepare a modified *Speedisk*™ by combing a one gram hydrophobic divinylbenzene (DVB) *Speedisk*™ and a one gram hydrophilic DVB *Speedisk*™. Remove the polypropylene mesh and wet the sorbent with methanol before combining *Speedisks*™. Cover the modified *Speedisk*™ with a polypropylene mesh.

6.3.2 Dry the modified Speedisk™ in a designated "clean" oven at 105°C for at least six hours.

6.4 When snow is melted, remove modified *Speedisks*™ from the oven, wait one hour, weigh them, and record weights in notebook.

6.5 Weigh each PTFE bag and record their weight in the notebook.

6.6 In a 7 mL vial, add 6 mL of methanol and the appropriate surrogates for the snow sample (see Table 1). Consult the laboratory standard notebook and calculate the desired concentration needed for the analysis. Shake vial to mix methanol and surrogates thoroughly.

6.7 Add 1 mL of the surrogate spike solution to each of the six PTFE bags. Rinse the 7 mL vial twice with methanol and add to one of the PTFE bags. Shake each PTFE bag for 30 seconds to ensure adequate mixing.

6.8 Assemble the Supelco Visiprep SPE Vacuum Manifold and mount the modified *Speedisks*™.

6.9 Condition the modified *Speedisks*™ by adding 15 mL of each of the following solvents to the disk holders. Before adding the next solvent on the list, draw all but ~1 mm of solvent through the disk at a flow rate of ~1 mL/second. Do not allow disks to become dry.

6.9.1 Ethyl Acetate (EA) [Used to wet the disk.]

6.9.2 DCM (Pull some through to remove the last solvent, then wait 1 minute to thoroughly allow solvent to soak the disk, then proceed.)

6.9.3 EA

6.9.4 Methanol (MeOH) (Pull some through to remove the last solvent, then wait 1 minute to thoroughly allow solvent to soak the disk, then proceed.)

6.9.5 Deionized (DI) water x 2 aliquots [to thoroughly remove the MeOH.]

6.10 Mount an extra speedisk holder (one that does not contain sorbent) on the manifold. Attach remote sample adapter to this extra speedisk holder. Clean remote sample adapter and tubing by drawing ~20 mL each of EA, DCM, MeOH, and DI water through.

6.11 Completely fill the modified *Speedisk*™ holders with DI water and attach the remote sample adapters. This allows excess water to purge the tubing of air.

Extraction of Analytes from Snow Sample Using Modified *Speedisks*™

6.12 With all of the air removed from the tubing of the first remote sample adapter, place the end of it's tubing into the first PTFE bag containing melted snow. Do the same for the second remote sample adapter and second PTFE bag. Tubing ends must remain under the surface of the water while the extraction process in underway.

6.13 When ready to begin the extraction, turn the vacuum on and record the time. Make sure that there are no leaks in the extraction apparatus (leaks will show in the form of air bubbles coming into the line). The flow rate through the extraction device will begin at ~200 mL/min and decrease with volume extracted.

6.14 When one bag is nearly empty, stop the vacuum and exchange PTFE bags. Extract the water in remaining PTFE bags. Record the extraction time and flow rate for each bag.

6.15 When extraction of the water in the sixth PTFE bag is nearly complete, add the residual water from the other bags to it.

6.16 When all the water has been extracted, add 40 mL of EA to the first PTFE bag. Close the top of the bag and shake for 30 seconds to extract analytes from the inside of the PTFE bag.

6.17 Transfer the EA to the second bag. Close the top of the bag and shake for 30 seconds. Pour the EA into a 150 mL beaker.

6.18 Repeat the two previous steps using new EA for the third/fourth bags and the fifth/sixth bags. Combine all EA used for rinsing bags.

6.19 Follow the PTFE bag cleaning steps outlined above using DCM:EA (1:1) and then DCM.

6.20 Dry the modified *Speedisk*™ by drawing air through it for 30 seconds.

Elution of Analytes from Modified *Speedisk*™

6.21 Assemble the manifold with 250 mL collection bottles beneath each modified *Speedisk*™.

6.22 Using the remote sample adapters, draw ~1 mL of the EA used for rinsing the PTFE bags through one of the modified *Speedisks*™. Allow the EA to soak in the disk for 30 seconds. Then, draw half of the EA through the disk. Repeat with the other disk. Use a flow rate of ~1 mL/second. Do not allow the disks to dry.

6.23 Repeat the process described above with the DCM:EA used to rinse the PTFE bags.

6.24 Repeat the process described above with the DCM used to rinse the PTFE bags.

6.25 Rinse the lines with ~20 mL of clean DCM.

6.26 Place the collection bottles in the freezer.

6.27 Dry the modified Speedisk™ in a designated "dirty" oven at 105°C overnight. Weigh and compare weight to that recorded before extraction to determine particulate mass in sample. Store disk for possible future analysis by wrapping in aluminum foil, placing in zip-lock bag, and placing in freezer.

Removal of Water from Sample

6.28 Remove samples from the freezer and allow them to thaw. If there is a water layer on top of the solvent layer, remove the water layer with a Pasteur pipette. Be careful not to remove any of the solvent.

6.29 Add ~30 mL of sodium sulfate to each 250 mL collection vial. Shake. If all of the sodium sulfate clumps, add more. The sodium sulfate is cleaned before use by the following procedure.

6.29.1 ASE program: Heat 5 min, Static 5 min, Flush 150%, Purge 240 sec, cycles 1. Use this program with DCM, then with EA.

6.29.2 Bake the sodium sulfate at 360°C for 12 hours.

Blow Down and Solvent Exchange to DCM

6.30 Transfer sample to tubes used in the Turbovap® II.

6.31 Adjust Turbovap® II pressure to 13 psi and the bath water temperature to 25°C.

6.32 Insert tubes into Turbovap® II and begin nitrogen blow down. Reduce loss of analyte to the tubes by rinsing sides with DCM.

6.33 Exchange the solvent to DCM by reducing volume to ~0.5 mL, adding ~10 mL of DCM, and then reducing volume to ~0.5 mL again. Repeat this procedure 4 times.

6.34 Reduce sample to ~0.2 mL.

Sample Clean Up by Gel Permeation Chromatography (GPC)

6.35 Attach a 0.45 µm Nylon syringe filter to a 1 mL gas-tight luer-lock syringe.

6.36 Transfer sample to the syringe barrel with a Pasteur pipette.

6.37 Depress syringe plunger and expel sample into a 0.7 mL GPC vial.

6.38 Rinse Turbovap® II tube several times. Transfer rinsate to filter and expel into GPC vial to obtain 0.7 mL in the GPC vial.

6.39 Use GPC to fractionate sample into a pre-analyte fraction (containing large-molecule interferences) and analyte-containing fraction.

6.40 Use blow down procedure described above to reduce pre-analyte fraction to ~0.5 mL. Store in 1 mL vial in fridge.

6.41 Prepare analyte-containing fraction for silica clean up by using blow down and solvent exchange procedure described above to reduce analyte-containing fraction to ~0.5 mL and exchange to hexane.

Sample Clean Up with Silica Solid-Phase Extraction (SPE) Cartridge

6.42 Assemble the vacuum manifold, clean the valves with solvents, insert clean stainless steel needle guides, mount a 20 g silica SPE cartridge, and place a bottle for waste solvent collection in the manifold.

6.43 Clean silica SPE cartridge.

6.43.1 Add 50 mL of EA to cartridge and draw all but ~1 mL through.

6.43.2 Add 50 mL of DCM to cartridge and draw all but ~1 mL through.

6.43.3 Add 50 mL of hexane to SPE. Draw hexane through the column until several drops are eluted. Allow column to sit until silica becomes translucent (~10 minutes).

6.44 Prepare column for sample by adding 75 mL of hexane to cartridge and drawing all but ~1 mL through.

6.45 Replace solvent waste bottle with clean bottle.

6.46 Add the sample and rinses of the Turbovap® II tube to the cartridge. Do not add more than 2 mL of sample plus rinsate.

6.47 Draw sample into cartridge until there is ~1 mm of sample remaining above the sorbent bed.

6.48 Add 50 mL of DCM to cartridge. Draw ~ 1 mL into cartridge and wait ~1 minute. Draw solvent through cartridge until there it is ~1 mm above sorbent bed.

6.49 Add 50 mL of DCM: EA (1:1) to cartridge. Draw solvent through cartridge, combining with DCM fraction, until around ~1 mm remains above sorbent bed. This is considered fraction 1.

6.50 Replace collection bottle with clean bottle.

6.51 Add 50 mL of EA to cartridge. Draw solvent through cartridge. This is considered fraction 2 and will be used only if analytes are not found in fraction 1.

6.52 Reduce volumes of fractions 1 and 2 to ~0.2 mL with the blow down procedure described previously and transfer to 0.5 mL inserts in 1 mL vials.

6.53 Before injection, spike samples with stable isotope labeled internal standards (see Table 1).

7.0 Sample Analysis and Data Interpretation

7.1 Each sample is analyzed on two different gas chromatographs equipped with mass spectrometers (MS). One MS utilizes electron impact (EI) as an ionization source and the other utilizes electron capture negative chemical ionization (ECNI).

7.2 The following SOPs describe data analysis protocols: "Standard Operating Procedure for GC/MS EI Sample Analysis" and "Standard Operating Procedure for GC/MS ECNI Sample Analysis".

8.0 Recovery

8.1 Four ~50-Kg snow samples were collected from the top of Mary's Peak, which is located ~40 km east of Corvallis, Oregon. Background concentrations were measured in one of these samples by analyzing it according to the method described in this SOP. The other three samples were analyzed by the method described in this SOP with the following exceptions. First, 1500 ng of each target analyte was spiked into the melted snow. Second, surrogates were not added to melted snow but rather to the final extract right before analysis. By quantifying target analytes against surrogates and subtracting background concentrations, percent recoveries across the entire method were determined.

8.2 Percent recoveries and percent relative standard deviations (%RSDs) for each target analyte are shown in Table 2.

9.0 Sample-Specific Estimated Detection Limits

9.1 Sample-specific estimated detection limits are calculated using the method described in EPA Method 8280A: *The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans by High Resolution Bas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)*. This method is described in detail in Section 11.3 in the WACAP Quality Assurance Project Plan (QAPP).

9.2 Sample-specific estimated detection limits are shown in Table 3 for a representative snow sample. This ~50-Kg sample was collected at Pear Lake in Sequoia National Park in March 2003.

Table 2: Target Recoveries Spiked at 30 ng/L for Snow Collected at Mary's Peak, Oregon

ECNI Target Analyte	Average % Recovery	%RSD
Trifluralin	33.6	12.7
Hexachlorobenzene	23.2	13.4
Chlorothalonil	NA	NA
Heptachlor	37.2	10.3
Dacthal	60.2	12.5
HCH, alpha	42.8	14.0
HCH, beta	58.5	18.2
HCH, gamma (Lindane)	56.4	14.0
HCH, delta	61.5	16.3
Triallate	56.8	16.8
Metribuzin	45.9	19.3
Aldrin	36.3	17.7
Chlorpyrifos oxon	NA	NA
Chlorpyrifos	58.6	12.8
Heptachlor epoxide	56.4	17.1
Chlordane, oxy	50.9	13.7
Chlordane, trans	55.3	11.0
Endosulfan I	56.7	16.1
Chlordane, cis	52.4	11.6
Nonachlor, trans	55.7	10.8
Dieldrin	50.7	12.5
PCB 52 (tetra)	NA	NA
PCB 74 (tetra)	49.8	20.9
PCB 101 (penta)	49.1	16.7
PCB 118 (penta)	48.2	17.2
Endrin	59.9	17.6
Endosulfan II	59.7	12.7
Nonachlor, cis	59.4	11.0
Endrin aldehyde	23.7	10.6
Endosulfan sulfate	62.3	13.5
PCB 153 (hexa)	50.9	15.0
PCB 138 (hexa)	54.6	14.2
PCB 187 (hepta)	55.6	13.5
PCB 183 (hepta)	55.5	13.4
Mirex	48.3	8.82

EI Target Analyte	Average % Recovery	%RSD
EPTC	13.1	9.89
Etridiazole	24.6	7.75
Pebulate	24.5	9.79
Acenaphthylene	16.2	15.47
Acenapthene	22.6	14.77
Fluorene	29.1	11.81
Phorate	NA	NA
Demeton	NA	NA
Propachlor	73.8	10.46
Atrazine desisopropyl	NA	NA
Atrazine desethyl	NA	NA
Carbofuran	NA	NA
Simazine	NA	NA
Prometon	NA	NA
Atrazine	34.6	44.79
Cyanazine	46.5	14.44
Phenanthrene	51.4	9.10
Anthracene	52.8	8.32
Diazinon	67.6	11.59
Disulfoton	31.0	6.92
Acetochlor	66.0	21.78
Alachlor	59.5	4.69
Metalochlor	70.5	5.74
Carbaryl	NA	NA
Malathion	51.3	6.78
Mehtyl Parathion	66.9	2.09
Parathion	NA	NA
Ethion	NA	NA
Fluoranthene	58.7	9.60
Pyrene	51.6	9.00
Retene	69.1	12.90
o,p'-DDE	53.9	11.13
p,p'-DDE	51.0	11.98
o,p'-DDD	71.8	11.08
p,p'-DDD	76.3	9.36
o,p'-DDT	50.2	11.22
p,p'-DDT	57.6	8.64
Methoxychlor	96.1	9.62
Benzo(a)anthracene	72.3	10.52
Chrysene + Triphenylene	66.8	12.12
Benzo(b)fluoranthene	67.7	11.31
Benzo(k)fluoranthene	67.8	12.17
Benzo(e)pyrene	71.3	11.65
Benzo(a)pyrene	59.9	10.54
Indeno(1,2,3-cd)pyrene	68.7	10.20
Dibenz(a,h)anthracene	70.7	11.20
Benzo(ghi)perylene	57.3	9.93

Table 3: Sample-Specific Detection Limits for Snow Collected at Pear Lake in Sequoia NP

ECNI Target Analyte	Sample-Specific Estimated Detection Limit (pg/L)
Trifluralin	0.74
Hexachlorobenzene	0.18
Chlorothalonil	151.17
Heptachlor	121.73
Dacthal	1.69
HCH, alpha	18.24
HCH, beta	32.10
HCH, gamma (Lindane)	12.30
HCH, delta	20.67
Triallate	10.08
Metribuzin	24.48
Aldrin	107.59
Chlorpyrifos oxon	70.86
Chlorpyrifos	6.86
Heptachlor epoxide	14.72
Chlordane, oxy	9.43
Chlordane, trans	0.42
Endosulfan I	4.85
Chlordane, cis	16.31
Nonachlor, trans	0.92
Dieldrin	105.64
PCB 52 (tetra)	3374.23
PCB 74 (tetra)	124.83
PCB 101 (penta)	31.02
PCB 118 (penta)	1.25
Endrin	47.56
Endosulfan II	2.02
Nonachlor, cis	0.56
Endrin aldehyde	23.16
Endosulfan sulfate	1.01
PCB 153 (hexa)	1.30
PCB 138 (hexa)	2.78
PCB 187 (hepta)	0.90
PCB 183 (hepta)	1.20
Mirex	27.08

EI Target Analyte	Sample-Specific Estimated Detection Limit (pg/L)
EPTC	45.02
Etridiazole	22.51
Pebulate	63.77
Acenaphthylene	19.81
Acenaphthene	11.25
Fluorene	8.25
Phorate	47.88
Demeton	558.65
Propachlor	3.68
Atrazine desisoproply	62.00
Atrazine desethyl	25.83
Carbofuran	N/A
Simazine	31.00
Prometon	34.63
Atrazine	11.48
Cyanazine	26.15
Phenanthrene	8.79
Anthracene	19.89
Diazinon	9.12
Disulfoton	197.80
Acetochlor	25.21
Alachlor	43.39
Metolachlor	13.83
Triallate	5.99
Carbaryl	N/A
Malathion	8.42
Methyl parathion	51.97
Parathion	3.18
Ethion	6.24
Fluoranthene	4.01
Pyrene	4.94
Retene	33.41
o,p'-DDE	24.66
p,p'-DDE	10.28
o,p'-DDD	24.66
p,p'-DDD	44.04
o,p'-DDT	23.42
p,p'-DDT	26.23
Methoxychlor	16.39
Benzo(a)anthracene	14.61
Chrys-L +Triph	13.32
Benzo(b)fluoranthene	6.85
Benzo(k)fluoranthene	4.98
Benzo(e)pyrene	8.93
Benzo(a)pyrene	7.90
Indeno(1,2,3-cd)pyrene	31.47
Dibenz(a,h)anthracene	28.85
Benzo(ghi)perylene	16.48

10.0 Initial Results

10.1 Concentrations of target SOCs that were measured in snow collected at Pear Lake in Sequoia National Park in March 2003 are shown in Table 4. Concentration ranges of SOCs measured in the European Alps are provided for comparison.

11.0 Pollution Prevention

11.1 When properly managed, the chemicals used in this method pose little threat to the environment.

11.2 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

12.0 Waste Management

12.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

12.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington DC, 20036.

13.0 Bibliography

13.1 EPA Method 3630C. Silica Gel Cleanup, Sections 7.3.1-7.3.4

13.2 J.T. Baker, Bakerbond Application Note, Extraction of EPA Method 525.2 Analytes from Water.

13.3 J.T. Baker, Bakerbond Application Note, Extraction of Organochlorine Pesticides Analytes from Water.

13.4 J.T Baker Catalog.

13.5 Standard Operating Procedure for GC/MS NCI Sample Analysis. Simonich Environ. Chem. Lab. Feb. 2003.

13.6 Standard Operating Procedure for GC/MS EI Sample Analysis. Simonich Environ. Chem. Lab. Feb. 2003.

Table 4: Initial Results

	Measured in Snow from Pear Lake in Sequoia NP (ng/L)	Measured in Snow from European Alps (ng/L)[1]
Chlordane, trans	0.012	
Chlorothalonil	3.1	
Chlorpyrifos	0.57	
Dacthal	1.8	
Dieldrin	4.5	
Endosulfan I	0.33	
Endosulfan II	0.41	
Endosulfan sulfate	0.14	
Hexachlorobenzene	0.015	
HCH, alpha	0.17	0.022-1.1 (Sum of alpha and beta)
HCH, beta	<QL	
HCH, gamma	0.044	
Methoxychlor	2.1	
Nonachlor, trans	0.17	
Nonachlor, cis	0.014	
Simazine	1.4	
DDTs	<QL	0.073-0.33
PCBs		0.2-2.2 (Sum of Seven Congeners)
PCB 52 (tetra)	<QL	
PCB 74 (tetra)	<QL	
PCB 101 (penta)	0.14	
PCB 118 (penta)	0.07	
PCB 153 (hexa)	0.10	
PCB 138 (hexa)	0.12	
PCB 187 (hepta)	0.038	
PCB 183 (hepta)	0.039	
PAHs		5.6-81 (Sum of 22 PAHs)
Phenanthrene	0.80	
Pyrene	0.49	
Retene	1.2	

[1] Carrera G., Fernandez P., Vilanova R.M., Grimalt J.O. (2001) Atmospheric Environment 35:245.

Standard Operating Procedure for the Determination of Semi-Volatile Organic Compounds in Lake Water Samples

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Sascha Usenko
January 2004

Standard Operating Procedure for the Determination of Semi-Volatile Organic Compounds in Lake Water Samples

Approvals:

Staci Simonich
Oregon State University
Principal Investigator

Staci I. Simonich 10/7/04
Signature *Date*

Dave Schmedding
Senior Research Assistant

10/11/04
Signature *Date*

Sascha Usenko
Graduate Research Assistant

Sascha Usenko 10/7/04
Signature *Date*

Standard Operating Procedure for the Determination of Semi-Volatile Organic Compounds in Lake Water Samples

Table of Contents:

1.0 Scope and Application

1.1 This method details the analytical method for the determination of semi-volatile organic compounds (SOCs) in lake water samples, after *Speedisk*™ and particulate filters return from the field site. Lake water extraction and filter procedure refer to the SOP "Standard Operating Procedure for the Extraction and Filtering of High Elevation Lake Water via the Infiltrex 100".

2.0 Summary of Method

2.1 A modified hydrophilic/hydrophobic divinylbenzene *Speedisk*™ containing a lake water extract will be removed from the storage freezer (*Speedisk*™ containing lake water extract can be stored for up to 10 days at -20°C) before the elution of target analytes (see Table 1) and spiked with the appropriate stable isotope labeled surrogates (see Table 1) in DCM. After the surrogate spike, the analytes of interest will be eluted from the *Speedisk*™ using the appropriate solvents. The glass fiber filter containing the particulate phase of the lake water sample will be removed from the storage freezer and transferred to a 100 mL accelerated solvent extractor (ASE) cell containing ~50 grams of sodium sulfate and spiked with the appropriate stable isotope labeled surrogates (see Table 1). After the filter has been spiked with surrogates, fill the remainder of the ASE cell with sodium sulfate and extract the contents of the cell using the ASE.

2.2 The eluate from both the *Speedisk*™ and ASE will be dried using sodium sulfate. Once dried, the extract will be reduced to 0.5 mL via nitrogen blow down and exchanged to hexane by solvent exchange. The 0.5 mL hexane extract will be added to the top of a 20-gram silica solid phase extraction (SPE) cartridge. Fractions will be collected individually using different combinations of solvents. The solvents will range in elution order from nonpolar to polar. Fractions containing analytes will be combined and reduced via nitrogen blow down to ~0.3 mL, depending on the concentration of the analytes and interferences in the extract.

2.3 The extract will be spiked just prior to injection with stable isotope labeled internal standards (see Table 1). Extracts will be analyzed for target compounds (see Table 1) with gas chromatographic (GC) mass spectrometry (MS). Two different ionization methods will be used, electron impact (EI) and negative chemical ionization (NCI), refer to the SOPs "Standard Operating Procedure for GC/MS EI Sample Analysis" and "Standard Operating Procedure for GC/MS NCI Sample Analysis", respectively.

Table 1. Target Compounds, Surrogates and Internal Standards

Electron Impact Ionization	Negative Chemical Ionization
PAHs: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene	**PCBs:** PCB 52 (2,2',5,5'-Tetrachlorobiphenyl), PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183 (2,2',3,4,4',5',6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl)
Pesticides and degradation products: o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon, Demeton S, Ethion, Etradiazole, Malathion*, Parathion and Methyl - Parathion, Phorate, Metolachlor, Methoxychlor, Acetochlor, Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine	**Pesticides and degradation products:** Hexachlorocyclohexanes (HCH) - α, β, γ(lindane), and - δChlordanes – cis, trans, oxy, Nonachlor – cis, trans, Heptachlor, , Heptachlor Epoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex, Polybrominated Diphenyl Ethers
Surrogates: *d10*-Fluorene, *d10*-Phenanthrene, *d10*-Pyrene, *d12*-Triphenylene, *d12*-Benzo[a]pyrene, *d12*-Benzo[ghi]perylene, *d14*-EPTC, *d10*-Phorate, *d5*-Atrazine, *d10*-Diazinon, *d7*-Malathion, *d10*-Parathion, *d8*-p,p'-DDE, *d8*-p,p'-DDT, *d6*-Methyl Parathion, *d13*-Alachlor, *d11*-Acetochlor	**Surrogates:** 13C12 PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), 13C12 PCB 180 (2,2', 3,4,4',5,5'-Heptachlorobiphenyl), *d10* - Chlorpyrifos, *13C6*-HCB, *d6*-γ-HCH, *d4*-Endosulfan I, *d4*-Endosulfan II
Internal Standards: *d10*-Acenaphthene, *d10*-Fluoranthene, *d12*-Benzo[k]fluoranthene	**Internal Standards:** *d14*-Trifluralin

3.0 Safety

3.1 The laboratory exhaust fume hood should be used when handling solvents.

3.2 Personal Protection Equipment (PPE) should be worn at all times during the procedure. Chemical resistant nitrile gloves should be worn when handling organic solvents. Eye protection should be worn when handling organic solvents and/or operating the manifold under the vacuum.

3.5 Material Safety Data Sheet (MSDS) reports for all solvents should be available in the laboratory.

4.0 Equipment and Supplies

4.1 A modified *Speedisk*™ containing 1 gram hydrophobic divinylbenzene (DVB) J.T. Baker *Speedisk*™ and 1 gram hydrophilic DVB J.T. Baker *Speedisk*™.

4.2 *Speedisk*™ Remote Sample Adapter

4.3 J.T. Baker Standard Vacuum Processor.

4.4 Varian Bond Elut® Silica Solid Phase Extraction Cartridge (20-gram).

4.5 Dionex sample insertion tool.

4.6 I-Chem 40 mL vial with open-top / PTFE resin/silicone septa (4 vials).

4.7 250 mL clear glass collection bottle with open-top / PTFE resin/silicone septa.

4.8 Forceps.

4.9 25 µL syringe.

4.10 Lab coat or apron.

4.11 Eye protection.

4.12 Nitrile gloves.

4.13 Laboratory exhaust fume hood.

5.0 Sample Handling and Storage

5.1 The transport of *Speedisk*™ and glass fiber filters will be documented in order to establish chain of custody. The chain of custody will document transport from the field site to the Simonich Environmental Chemical Laboratory (SECL) located on Oregon State University in Corvallis.

5.2 All *Speedisk*™ and glass fiber filters will be kept in coolers with dry ice during transportation. Transportation is the responsibilities of SECL or USEPA.

Speedisk™ and glass fiber filters will be stored in freezers kept at –20°C ± 5°C (up to 10 days) until time of extraction. After extraction, extracts will be stored in a refrigerator kept at 10°C ± 5°C.

6.0 *Speedisk*™ Procedures

Setup and Surrogate Spike of a *Speedisk*™

6.1 Set up the J.T. Baker Standard Vacuum Processor (12-port manifold) with clean stopcocks and stainless needle flowpath liner.

6.2 Assemble the manifold with a 250 mL collection bottle. If elution volume exceeds 200 mL, swap with a new 250 mL collection bottle.

6.3 Attach vacuum to manifold and check vacuum pressure. Do not exceed manufacturer's maximum vacuum pressure. Opening and closing the stopcock can control flow rates for the SPE.

6.4 Mount the modified *Speedisk*™ used to extract a lake water sample to a vacuum port on the vacuum manifold.

Note: A modified *Speedisk*™ contains a 1 gram hydrophobic divinylbenzene (DVB) *Speedisk*™ and a 1 gram hydrophilic DVB *Speedisk*™.

6.5 Turn on the vacuum (typical vacuum pressure is ~20 inches mercury), but do not apply the vacuum to the *Speedisk*™.

6.6 In a 7 mL vial, add ~3 mL of dichloromethane (DCM) and the appropriate surrogates for spiking the *Speedisk*™ (see Table 1). Consult the laboratory standard notebook and calculate the desired concentration need for the analysis. Mix the DCM and surrogates thoroughly.

6.7 Add the DCM surrogate solution (from the 7 mL vial) to the *Speedisk*™. Rinse the 7 mL vial twice (~1 mL each) with DCM and add it to the *Speedisk*™.

6.8 After the surrogate spike, pull the surrogate solution into the *Speedisk*™ via the vacuum and allow it to soak the *Speedisk*™ for 30-45 seconds.

Sample Elution of *Speedisk*™

6.9 Elute the *Speedisk*™ with three rinses of the following solvents: DCM, ethyl acetate (EA):DCM (1:1), and EA respectively. Each solvent rinse should be roughly ~25 mL. Pull a few drops through the sorbent bed, then stop the vacuum and soak the disk for ~1 minute. Pull through the remaining solvent and continue to the next elution solvent until this step is complete.

Removal of Water from Extracts

6.10 All extracts will be dried using sodium sulfate in a 10-inch disposable glass column.

6.11 Place glass wool in the bottom of a 12 inch disposable glass column. Clean the column and the glass wool with three rinses of EA, DCM and hexane (nine total).

6.12 Fill the column ~70% full with sodium sulfate, ~30 grams (sodium sulfate should be pre-cleaned via solvent extracted in the ASE with DCM and EA before use and bake at 450°C for 6 hrs).

6.13 Pour extract through slowly and collect in a 250 mL collection bottle. (Check sample for cloudiness, droplets, or any other signs of water.) Repeat these steps with fresh sodium sulfate until solvent shows no signs of water (cloudiness and/or water droplets).

6.14 Rinse the funnel and column (including sodium sulfate) with two (5 to 10 mL) rinses of the following solvents DCM, EA:DCM (1:1), and EA. This helps reduce loss of analyte on the glassware and sodium sulfate.

Blow Down and Solvent Exchange

6.15 Once the extract has been dried, reduce the sample volume via nitrogen blow-down in a Turbovap® II. Set the Turbovap® II for 13 psi and the bath water temperature of ~25°C.

6.16 While the extract is being reduced, rinse the Turbovap® tube down with DCM and hexane. This helps reduce loss of analyte on the side wall of the Turbovap® tube.

6.17 Reduce the extract down to ~0.5 mL and begin solvent exchange into hexane via the Turbovap® II. Solvent exchange may take 4-5 steps of adding hexane and reducing down via nitrogen blow-down.

Cleaning and Conditioning of the Silica SPE

6.18 Assemble the manifold with clean stopcocks, stainless steel needle flowpath liners, and two 250 mL collection bottles. The stopcocks and stainless steel needle flowpath liners are cleaned a beaker with various solvents in a sonicator bath.

6.19 Obtain a 20-gram silica solid phase extraction (SPE) cartridge.

6.20 Turn on the vacuum pump and set pump vacuum to 7.5 inches of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum.

6.21 Clean the SPE cartridge with 100 mL of EA, DCM, and hexane. Pull a few drops through the sorbent bed and then allowed to soak for 1 minute, before pulling the rest of the solvent through the SPE.

6.22 Condition the column by adding 75 mL of hexane. Pull a few drops of hexane through the column then let sit until silica becomes translucent before proceeding (~10 min). After silica is translucent pull the remaining 75 mL of hexane through the column, until meniscus is ~1-2 mm above the sorbent bed.

Purification of the Extract

6.23 Add the roughly ~0.5 mL extract to the top of the SPE. Rinse vial twice with ~0.5 mL of hexane and add to the SPE.

6.24 Pull through extract until at least 1 mm of solvent above the sorbent bed.

6.25 For fraction one, pour 100 mL of EA: DCM (1:1) onto the SPE and collect fraction in the first 250 mL collection bottle.

6.26 Pull ~1 mL through and allow solvent to soak the SPE for 1 minute. Then pull the remaining solvent at 2 mL per minute until meniscus is ~1-2 mm above the SPE.

6.27 For fraction two, repeat steps 6.25 + 6.26 with 50 mL of EA. Collect fraction in second 250 mL collection bottle. Store in a refrigerator kept at 10°C ± 5°C for storage. This may be used later on if analytes were not collected in the first fraction.

6.28 Blow down fraction 1 to ~0.5 mL using the same Turbovap® II method as stated above.

6.29 Prior to injection spike the extract with stable isotope labeled internal standards (see Table 1).

7.0 Particulate Filter Procedure

7.1 Pre-clean one 100 mL stainless steel ASE cell and two stainless steel caps with Acetone, EA, DCM, and Hexane for each filter being extracted.

Note: Make sure that the caps have a good PEEK seal and frit. Also make sure that the 100 mL ASE cell has no major nicks along ends.

7.2 Remove the 1 µm particulate glass fiber filter (140 mm diameter) containing the particulate phase of the lake water sample from the storage freezer.

Note: Filter should be stored in a 40 mL VOA vial with Teflon septum.

7.3 Screw on one cap and push a 1 µm glass fiber filter (30 mm) down the inside of the cell to the bottom with the Dionex filter insertion tool.

7.4 Place ~50 grams of pre-cleaned sodium sulfate into the ASE cell.

Note: Pre-clean sodium sulfate in ASE with one rinse of DCM and EA, then bake at 450°C for 6 hrs).

7.5 Remove the particulate filter from the VOA vial with clean forceps and place it in the ASE cell on top of the 50 grams of sodium sulfate.

7.6 Fill the remainder of the ASE cell with sodium sulfate. Use the filter insertion tool to pack the sodium sulfate around the particulate filter.

Note: Packing the filter forces water out of the filter and into the sodium sulfate.

7.7 Screw the top cap onto the ASE cell and place in the ASE.

7.8 Extract the particulate filter at 100°C and 1500 psi with DCM and then EA using the ASE. Note: Extracts will be collected separately in two different 250 mL collection bottles.

7.9 The DCM and EA extracts will be combined, and then taken through steps 6.10 – 6.29 of the *Speedisk*™ procedure before analysis.

8.0 Extract Analysis and Data Interpretation

8.1 Analyze samples extracts (*Speedisk*™ and particulate filter) for target compounds (see Table 1) with GC/EI-MS and GC/ECNI-MS

8.2 Data Analysis for extracts run on GC/MS EI, refer to the SOP "Standard Operating Procedure for GC/MS EI Sample Analysis".

8.3 Data Analysis for extracts run on GC/MS NCI, refer to the SOP "Standard Operating Procedure for GC/MS NCI Sample Analysis".

9.0 Pollution Prevention

9.1 The chemicals used in this method pose little threat to the environment.

9.2 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

10.0 Waste Management

10.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench

operations. Compliance with all sewage discharge permits and regulations is also required.

10.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington DC, 20036.

11.0 References

11.1 EPA Method 3630C. Silica Gel Cleanup, Sections 7.3.1-7.3.4

11.2 J.T. Baker, Bakerbond Application Note, Extraction of EPA Method 525.2 Analytes from Water.

11.3 J.T. Baker, Bakerbond Application Note, Extraction of Organochlorine Pesticides Analytes from Water.

11.4 J.T Baker Catalog.

11.5 Standard Operating Procedure for GC/MS NCI Sample Analysis. Simonich Environ. Chem. Lab. Feb. 2003.

11.6 Standard Operating Procedure for GC/MS EI Sample Analysis. Simonich Environ. Chem. Lab. Feb. 2003.

Standard Operating Procedure for GC/MS EI Sample Analysis

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Glenn Wilson
Version 1.1
January 2004

Standard Operating Procedure for
GC/MS EI Sample Analysis

Approvals:

Staci Simonich
Oregon State University
Principal Investigator

Staci L. Simonich 10/7/04
Signature *Date*

Dave Schmedding
Senior Research Assistant

[signature] 10/11/04
Signature *Date*

Glenn Wilson
Research Assistant

Glenn Wilson 10-11-04
Signature *Date*

Standard Operating Procedure for GC/MS EI Sample Analysis

Table of Contents:

1.0 Scope and Application

1.1 This method details the procedure for analysis of samples using the Gas Chromatograph/Mass Selective Detector Electron Impact (GC/MS EI) instrument. This instrument is an Agilent 5973 MSD equipped with a J&W 30 meter x .25mm x .25um DB5-MS column.

2.0 Summary of Method

2.1 This check assumes the GC/MS is within normal operational parameters. Also assumed is that the operator is familiar with the operation of the instrument. First, decafluorotriphenylphosphine (DFTPP) is injected as a quick test for instrument operation and sensitivity. Secondly, a daily standard is run to ensure the fitness of the instrument for the analysis being performed. Lastly, the samples will be run.

3.0 Run and evaluate DFTPP

3.1 Make sure the solvent rinse vials in the autosampler turret are filled. The "solvent a" should be acetone, and "solvent b" and "solvent b2" should be dichloromethane (DCM).

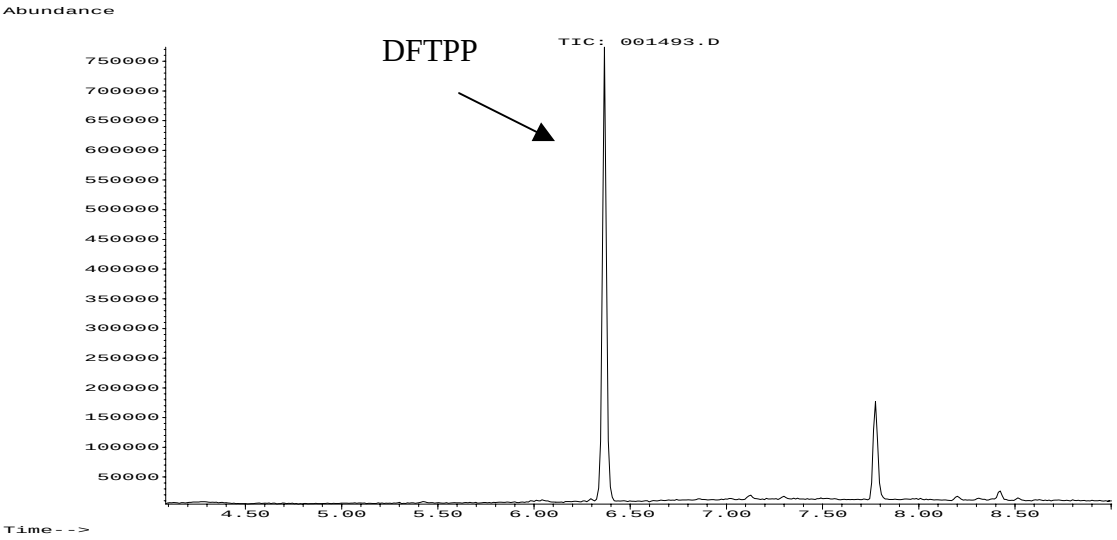
3.2 Raise the GC column oven temperature to about 300 degrees C if it has not been used recently, or has been used with dirty samples. The purpose of the high oven temperature is to elute compounds that have collected on the GC column. Typically, five to ten minutes at 300 degrees C should be sufficient.

3.3 Make a run sequence and run the 10 ng/µl DFTPP standard. Be sure to fill out the instrument run logbook. The current run method is DFT02.

3.4 Evaluate the run when it is finished. The peak height should be near one million counts. The degradation (later) peak should be less than 25% of the main (first) peak. The baseline should be relatively low and clean. If these conditions are not met, rerun the DFTPP aliquot. If the second run does not appear good, try to determine the origin of the problem. A poor run may be due to earlier runs of dirty samples, old standards, incorrect solvents, or a corrupted run method. Seek help if the problem is not resolved. Changing an injection liner or clipping the column may be required to obtain satisfactory instrument performance.

3.5 When the DFTPP run is judged to be satisfactory, proceed to running a daily run standard.

3.6 See Section 9.0 for the DFTPP GC/MS run parameters.



4.0 Run and evaluate a standard of target SOCs

4.1 Make sure the solvent rinse vials in the autosampler turret are filled. The "solvent a" should be acetone, and "solvent b" and "solvent b2" should be compatible with the solvent used in the standard to be run.

4.2 Make a run sequence and run the standard. Be sure to fill out the instrument run logbook. The sample aliquot should be either a midpoint in the calibration curve, or a daily control standard generated with the sample to be run. The SIM method is OC02ESM. See Section 10.0 for the method parameters. Table 1 lists the SOCs that are analyzed by electron impact ionization.

4.3 When the run is completed, quant and qedit the run. Pay attention to retention times, spectral data and other qualifying information to determine correct compound identification. Be sure all compounds are present. There may be a need to adjust SIM windows if the column has been cut. Some compounds may be seen only partially if window assignments are incorrect. If this is so, run the standard on the full scan acquisition method so that window assignments may be evaluated. The full scan method is OC02. See appendix C for the method parameters. The compounds are the same as those listed above in section 4.2.

4.4 Rerun and evaluate the daily standard with the SIMS method if adjustments were made to window times.

Table 1. SOCs Analyzed by Electron Impact Ionization

PAHs: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene

Pesticides and degradation products: o,p'-DDT*, p,p'-DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon, Demeton S, Ethion, Etradiazole, Malathion*, Parathion and Methyl - Parathion, Phorate, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine

Surrogates: d_{10}-Fluorene, d_{10}-Phenanthrene, d_{10}-Pyrene, d_{12}-Triphenylene, d_{12}-Benzo[a]pyrene, d_{12}-Benzo[ghi]perylene, d_{14}-EPTC, d_{10}-Phorate, d_5-Atrazine, d_{10}-Diazinon, d_7-Malathion, d_{10}-Parathion, d_8-p,p'-DDE, d_8-p,p'-DDT, d_6-Methyl Parathion, d_{13}-Alachlor, d_{11}-Acetochlor

Internal Standards: d_{10}-Acenaphthene, d_{10}-Fluoranthene, d_{12}-Benzo[k]fluoranthene

5.0 Run the Samples

5.1 Evaluate the samples to determine if they need pre-screening on the gas chromatograph/flame ionization detector (GC/FID). For example, samples that are very viscous or highly colored would be pre-screened on the GC/FID.

5.2 Make a sequence and run the samples using the SIMS method OC02ESM.

6.0 GC/MS Data Analysis

6.1 Overview- The sample data is loaded, the appropriate method is loaded, and the sample is quantified using a calibration previously established. After quantification, the sample is edited to ensure quality. The following section goes

through the steps used in this process. The **bold** indicates the menu choice which is left clicked with the mouse.

6.2 Loading the data file- Select **View, Data Analysis, File, Load Data File**.

6.3 Loading the method- Select **File, Load Method,(Method Name)**

6.4 To quantify- Select **Quant, Calculate**.

6.5 To edit- Select **Quant, Qedit**.

7.0 Pollution Prevention

7.1 The chemicals used in this method pose little threat to the environment.

7.2 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

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8.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

8.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington DC, 20036.

9.0 GC/EI-MS parameters for DFTPP analysis

INSTRUMENT CONTROL PARAMETERS

Sample Inlet: GC
Injection Source: GC ALS
Mass Spectrometer: Enabled

==========

6890 GC METHOD

==========

OVEN
Initial temp: 150 'C (On) Maximum temp: 325 'C
Initial time: 1.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	20.00	240	2.00
2	20.00	320	4.00
3	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 15.50 min

FRONT INLET (UNKNOWN) BACK INLET ()
Mode: Pulsed Splitless
Initial temp: 250 'C (On)
Pressure: 12.86 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 0.60 min
Purge flow: 20.0 mL/min
Purge time: 0.50 min
Total flow: 24.1 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 1.00 min
Gas type: Helium

COLUMN 1 COLUMN 2
Capillary Column (not installed)
Model Number: Agilent 122-5532
DB-5ms, 0.25mm * 30m * 0.25um
Max temperature: 350 'C
Nominal length: 29.5 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 12.96 psi
Average velocity: 38 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET) BACK DETECTOR (NO DET)

SIGNAL 1 SIGNAL 2
Data rate: 20 Hz Data rate: 20 Hz
Type: test plot Type: test plot
Save Data: Off Save Data: Off
Zero: 0.0 (Off) Zero: 0.0 (Off)
Range: 0 Range: 0
Fast Peaks: Off Fast Peaks: Off
Attenuation: 0 Attenuation: 0

COLUMN COMP 1 COLUMN COMP 2
(No Detectors Installed) (No Detectors Installed)

THERMAL AUX 2
Use: MSD Transfer Line Heater
Description:
Initial temp: 280 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes 1
Sample Pumps 4
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 2
PostInj Solvent B Washes 2
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:
No parameters specified

MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File : MT07.U
Acquistion Mode : Scan

MS Information
-- -----------

Solvent Delay : 4.00 min

EM Absolute : True
Resulting EM Voltage : 1552.9

[Scan Parameters]

Low Mass : 45.0
High Mass : 500.0
Threshold : 50
Sample # : 3 A/D Samples 8

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 200 C maximum 250 C

10.0 GC/EI-MS parameters for target SOC analysis

INSTRUMENT CONTROL PARAMETERS

Sample Inlet: GC
Injection Source: GC ALS
Mass Spectrometer: Enabled

==========

6890 GC METHOD

==========

OVEN
Initial temp: 60 'C (On) Maximum temp: 325 'C
Initial time: 1.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	6.00	300	3.00
2	20.00	320	9.00
3	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 54.00 min

FRONT INLET (UNKNOWN) BACK INLET ()
Mode: Pulsed Splitless
Initial temp: 300 'C (On)
Pressure: 7.80 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 0.60 min
Purge flow: 20.0 mL/min
Purge time: 0.50 min
Total flow: 24.2 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 1.00 min
Gas type: Helium

COLUMN 1 COLUMN 2
Capillary Column (not installed)

Model Number: Agilent 122-5532
DB-5ms, 0.25mm * 30m * 0.25um
Max temperature: 350 'C
Nominal length: 29.5 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 7.80 psi
Average velocity: 37 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET) BACK DETECTOR (NO DET)

SIGNAL 1
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 2
Use: MSD Transfer Line Heater
Description:
Initial temp: 300 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes 0
Sample Pumps 4
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 4
PostInj Solvent B Washes 2
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:
No parameters specified

MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File : MT07.U
Acquistion Mode : SIM

MS Information
-- -----------

Solvent Delay : 6.00 min

EM Absolute : True
Resulting EM Voltage : 1752.9

[Sim Parameters]

GROUP 1
Group ID : 1
Resolution : Low
Plot 1 Ion : 128.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(128.0, 30) (132.0, 30) (142.0, 30)
(189.0, 30) (203.0, 30)

GROUP 2
Group ID : 2

Resolution : Low
Group Start Time : 16.55
Plot 1 Ion : 183.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(183.0, 40) (211.0, 40) (213.0, 40)

GROUP 3
Group ID : 3
Resolution : Low
Group Start Time : 17.01
Plot 1 Ion : 76.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(76.0, 30) (128.0, 30) (151.0, 30)
(152.0, 30) (161.0, 30) (203.0, 30)

GROUP 4
Group ID : 4
Resolution : Low
Group Start Time : 17.50
Plot 1 Ion : 152.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(152.0, 30) (153.0, 30) (154.0, 30)
(162.0, 30) (164.0, 30)

GROUP 5
Group ID : 5
Resolution : Low
Group Start Time : 19.40
Plot 1 Ion : 163.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(163.0, 30) (165.0, 30) (166.0, 30)
(174.0, 30) (176.0, 30)

GROUP 6
Group ID : 6
Resolution : Low
Group Start Time : 20.02
Plot 1 Ion : 93.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(93.0, 30) (120.0, 30) (176.0, 30)

GROUP 7
Group ID : 7
Resolution : Low
Group Start Time : 20.60

Plot 1 Ion : 158.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(158.0, 30) (172.0, 30) (173.0, 30)
(174.0, 30) (175.0, 30) (187.0, 30)

GROUP 8
Group ID : 8
Resolution : Low
Group Start Time : 21.46
Plot 1 Ion : 121.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(121.0, 30) (131.0, 30) (231.0, 30)
(260.0, 30) (270.0, 30)

GROUP 9
Group ID : 9
Resolution : Low
Group Start Time : 22.15
Plot 1 Ion : 88.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(88.0, 30) (170.0, 30) (258.0, 30)

GROUP 10
Group ID : 10
Resolution : Low
Group Start Time : 22.60
Plot 1 Ion : 131.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(131.0, 10) (149.0, 10) (164.0, 10)
(183.0, 10) (186.0, 10) (200.0, 10)
(201.0, 10) (202.0, 10) (203.0, 10)
(205.0, 10) (210.0, 10) (215.0, 10)
(220.0, 10) (225.0, 10)

GROUP 11
Group ID : 11
Resolution : Low
Group Start Time : 23.20
Plot 1 Ion : 138.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(88.1, 20) (89.1, 20) (138.0, 20)
(176.0, 20) (178.0, 20) (179.0, 20)
(186.0, 20) (188.0, 20) (189.0, 20)
(199.0, 20) (304.0, 20) (314.0, 20)

GROUP 12
Group ID : 12
Resolution : Low
Group Start Time : 24.00
Plot 1 Ion : 86.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(86.0, 40) (268.0, 40) (270.0, 40)

GROUP 13
Group ID : 13
Resolution : Low
Group Start Time : 24.65
Plot 1 Ion : 146.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(146.0, 30) (162.0, 30) (173.0, 30)
(223.0, 30) (245.0, 30)

GROUP 14
Group ID : 14
Resolution : Low
Group Start Time : 25.11
Plot 1 Ion : 109.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(109.0, 15) (115.0, 15) (125.0, 15)
(160.0, 15) (188.0, 15) (200.0, 10)
(237.0, 15) (251.0, 15) (263.0, 15)
(269.0, 15)

GROUP 15
Group ID : 15
Resolution : Low
Group Start Time : 25.50
Plot 1 Ion : 115.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(115.0, 40) (116.0, 40) (144.0, 40)

GROUP 16
Group ID : 16
Resolution : Low
Group Start Time : 26.35
Plot 1 Ion : 127.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(127.0, 30) (131.0, 30) (158.0, 30)
(162.0, 30) (173.0, 30) (174.0, 30)
(238.0, 30) (240.0, 30)

GROUP 17
Group ID : 17
Resolution : Low
Group Start Time : 26.72
Plot 1 Ion : 109.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(109.0, 30) (115.0, 30) (155.0, 30)
(225.0, 30) (227.0, 30) (240.0, 30)
(291.0, 30)

GROUP 18
Group ID : 18
Resolution : Low
Group Start Time : 28.00
Plot 1 Ion : 200.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(200.0, 40) (202.0, 40) (203.0, 40)
(212.0, 40) (213.0, 40)

GROUP 19
Group ID : 19
Resolution : Low
Group Start Time : 28.60
Plot 1 Ion : 316.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(316.0, 40) (318.0, 40) (320.0, 40)

GROUP 20
Group ID : 20
Resolution : Low
Group Start Time : 28.96
Plot 1 Ion : 200.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(200.0, 40) (202.0, 40) (203.0, 40)
(212.0, 40) (213.0, 40)

GROUP 21
Group ID : 21
Resolution : Low
Group Start Time : 29.65
Plot 1 Ion : 315.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(165.1, 40) (235.0, 40) (237.0, 40)
(315.9, 40) (317.9, 40) (319.9, 40)

(324.0, 40) (326.0, 40)

GROUP 22
Group ID : 22
Resolution : Low
Group Start Time : 30.35
Plot 1 Ion : 204.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(204.0, 40) (219.0, 40) (234.0, 40)

GROUP 23
Group ID : 23
Resolution : Low
Group Start Time : 31.10
Plot 1 Ion : 165.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(153.0, 40) (165.0, 40) (231.0, 40)
(235.0, 40) (237.0, 40) (243.0, 40)
(245.0, 40) (384.0, 40)

GROUP 24
Group ID : 24
Resolution : Low
Group Start Time : 33.70
Plot 1 Ion : 226.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(226.0, 30) (227.0, 30) (228.0, 30)
(229.0, 30) (240.0, 30) (241.0, 30)
(270.0, 30)

GROUP 25
Group ID : 25
Resolution : Low
Group Start Time : 37.60
Plot 1 Ion : 250.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(250.0, 40) (252.0, 40) (253.0, 40)
(264.0, 40) (265.0, 40)

GROUP 26
Group ID : 26
Resolution : Low
Group Start Time : 42.00
Plot 1 Ion : 274.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(274.0, 40) (276.0, 40) (277.0, 40)
(278.0, 40) (279.0, 40)

GROUP 27
Group ID : 27
Resolution : Low
Group Start Time : 43.00
Plot 1 Ion : 274.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(274.0, 40) (276.0, 40) (277.0, 40)
(288.0, 40) (289.0, 40)

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 200 C maximum 250 C

Compound List Report MSD A

Method : D:\MSDCHEM\1\METHODS\OC02GSM.M (RTE Integrator)
Title : NPS analytes full scan EI
Last Update : Tue Jun 24 08:31:29 2003
Response via : Initial Calibration
Total Cpnds : 136

PK#		Compound Name	QIon	Exp_RT	Rel_RT	Cal	#Qual	A/H	ID
1	I	Acenaphthene-d10	164	18.65	1.000	L	1	A	B
2	S	EPTC-d14	142	15.75	0.844	A	1	A	B
3	S	Fluorene-d10	176	20.71	1.110	A	1	A	B
4	S	Phorate-d10	131	22.64	1.214	A	1	A	B
5	S	Atrazine-d5	205	23.76	1.274	A	1	A	B
6	S	Phenanthrene-d10	188	24.46	1.311	A	1	A	B
7	S	Diazinon-d10	314	24.45	1.311	A	1	A	B
8	I	Fluoranthene-d10	212	29.16	1.000	A	1	A	B
9	S	Acetochlor-d11	173	25.92	0.889	A	1	A	B
10	S	Methyl parathion-d6	269	26.21	0.899	A	1	A	B
11	S	Alachlor-d13	200	26.17	0.898	A	1	A	B
12	S	Malathion-d7	174	27.41	0.940	A	1	A	B
13	S	Parathion-d10	115	27.79	0.953	A	0	A	B
14	S	Pyrene-d10	212	30.00	1.029	A	1	A	B
15	S	p,p'-DDE-d8	326	30.84	1.058	A	1	A	B
16	I	Benzo(k)fluoranthene-d12	264	38.84	1.000	A	1	A	B

17	S	p,p'-DDT-d8	243	33.31	0.858	A	1	A	B	
18	S	Triphenylene-d12	240	34.84	0.897	A	1	A	B	
19	S	Benzo(a)pyrene-d12	264	39.79	1.024	A	1	A	B	
20	S	Benzo(ghi)perylene-d12	288	44.19	1.138	A	1	A	B	
21	I	Acenaphthene-d10-IS	164	18.65	1.000	L	1	A	B	
22	T	EPTC	128	15.95	0.855	L	2	A	B	
23	T	Etridiazole	211	17.92	0.961	L	2	A	B	
24	T	Acenaphthylene	152	18.07	0.969	L	2	A	B	
25	T	Pebulate	128	18.22	0.977	L	2	A	B	
26	T	Acenaphthene	154	18.77	1.006	L	2	A	B	
27	T	Fluorene	166	20.82	1.116	L	2	A	B	
28	T	Propachlor	120	21.11	1.132	L	2	A	B	
29	T	Atrazine desisopropyl	173	21.85	1.171	L	2	A	B	
30	T	Atrazine desethyl	172	22.09	1.184	L	2	A	B	
31	T	Phorate	260	22.78	1.221	L	2	A	B	
32	T	Demeton-S	88	23.41	1.255	L	2	A	B	
33	T	Carbofuran	164	23.57	1.264	L	2	A	B	
34	T	Simazine	201	23.66	1.268	L	2	A	B	
35	T	Prometon	210	23.70	1.270	L	2	A	B	
36	T	Atrazine	200	23.83	1.278	L	2	A	B	
37	T	Phenanthrene	178	24.55	1.316	L	2	A	B	
38	T	Diazinon	304	24.58	1.318	L	2	A	B	
39	T	Anthracene	178	24.75	1.327	L	2	A	B	
40	T	Disulfoton	88	24.88	1.334	L	2	A	B	
41	I	Fluoranthene-d10-IS	212	29.16	1.000	L	1	A	B	
42	T	Triallate	268	25.14	0.862	L	2	A	B	
43	T	Acetochlor	146	26.06	0.894	L	2	A	B	
44	T	Methyl parathion	263	26.29	0.902	L	2	A	B	
45	T	Alachlor	188	26.33	0.903	L	2	A	B	
46	T	Carbaryl	144	26.43	0.906	L	2	A	B	
47	T	Malathion	173	27.50	0.943	L	2	A	B	
48	T	Metolachlor	162	27.59	0.946	L	2	A	B	
49	T	Cyanazine	225	27.81	0.954	L	2	A	B	
50	T	Parathion	291	27.93	0.958	L	2	A	B	
51	T	Fluoranthene	202	29.23	1.002	L	2	A	B	
52	T	o,p' DDE	318	29.86	1.024	L	2	A	B	
53	T	Pyrene	202	30.06	1.031	L	2	A	B	
54	T	p,p' DDE	318	30.90	1.060	L	2	A	B	
55	T	o,p' DDD	235	31.09	1.066	L	2	A	B	
56	T	Retene	219	31.49	1.080	L	2	A	B	
57	T	p,p' DDD	235	32.21	1.104	L	2	A	B	
58	I	Benzo(k)fluoranthene-d12-IS	264	38.84	1.000	L	1	A	B	

59	T	o,p' DDT	235	32.27	0.831	L	2	A	B
60	T	Ethion	231	32.25	0.830	L	2	A	B
61	T	p,p' DDT	235	33.38	0.859	L	2	A	B
62	T	Benzo(a)anthracene	228	34.87	0.898	L	2	A	B
63	T	Chrys + Triph	228	34.99	0.901	L	2	A	B
64	T	Methoxychlor	227	35.11	0.904	L	2	A	B
65	T	Benzo(b)fluoranthene	252	38.81	0.999	L	2	A	B
66	T	Benzo(k)fluoranthene	252	38.90	1.002	L	2	A	B
67	T	Benz(e)pyrene	252	39.69	1.022	L	2	A	B
68	T	Benzo(a)pyrene	252	39.86	1.026	L	2	A	B
69	T	Indeno(1,2,3-cd)pyrene	276	43.41	1.118	L	2	A	B
70	T	Dibenz(a,h)anthracene	278	43.57	1.122	L	2	A	B
71	T	Benzo(ghi)perylene	276	44.29	1.140	L	2	A	B
72	I	EPTC-d14-LS	142	15.75	1.000	L	1	A	B
73	T	EPTC-LA	128	15.95	1.013	L	2	A	B
74	T	Etridiazole-L	211	17.92	1.138	L	2	A	B
75	T	Pebulate-L	128	18.22	1.156	L	2	A	B
76	I	Fluorene-d10-LS	176	20.71	1.000	L	1	A	B
77	T	Acenaphthylene-L	152	18.07	0.872	L	1	A	B
78	T	Acenaphthene-L	154	18.77	0.907	L	2	A	B
79	T	Fluorene-LA	166	20.82	1.005	L	2	A	B
80	I	Phorate-d10-LS	131	22.64	1.000	L	1	A	B
81	T	Phorate-LA	260	22.78	1.006	L	2	A	B
82	T	Demeton-S-L	88	23.41	1.034	L	1	A	B
83	I	Atrazine-d5-LS	205	23.76	1.000	L	1	A	B
84	T	Propachlor-L	120	21.11	0.888	L	2	A	B
85	T	Atrazine desisoproply-L	173	22.08	0.929	L	1	A	B
86	T	Atrazine desethyl-L	172	22.09	0.929	L	2	A	B
87	T	Carbofuran-L	164	23.62	0.994	L	2	A	B
88	T	Simazine-L	201	23.66	0.995	L	2	A	B
89	T	Prometon-L	210	23.70	0.997	L	2	A	B
90	T	Atrazine-LA	200	23.83	1.003	L	2	A	B
91	T	Cyanazine-L	225	27.81	1.170	L	2	A	B
92	I	Phenanthrene-d10-LS	188	24.46	1.000	L	1	A	B
93	T	Phenanthrene-LA	178	24.75	1.012	L	2	A	B
94	T	Anthracene-L	178	24.75	1.012	L	2	A	B
95	I	Diazinon-d10-LS	314	24.45	1.000	L	1	A	B
96	T	Diazinon-LA	304	24.58	1.005	L	2	A	B
97	T	Disulfoton-L	88	24.88	1.017	L	2	A	B

98	I	Acetochlor-d11-LS	173	25.92	1.000	L	1	A B
99	T	Acetochlor-LA	146	26.06	1.005	L	2	A B
100	I	Alachlor-d13-LS	200	26.17	1.000	L	1	A B
101	T	Alachlor-LA	188	26.33	1.006	L	2	A B
102	T	Metolachlor-L	162	27.59	1.054	L	2	A B
103	I	Malathion-d7-LS	174	27.41	1.000	L	1	A B
104	T	Triallate-L	268	25.14	0.917	L	1	A B
105	T	Carbaryl-L	144	26.43	0.964	L	2	A B
106	T	Malathion-LA	173	27.50	1.003	L	2	A B
107	I	Methyl parathion-d6-LS	269	26.21	1.000	L	1	A B
108	T	Methyl parathion-LA	263	26.29	1.003	L	2	A B
109	I	Parathion-d10-LS	115	27.80	1.000	L	0	A B
110	T	Parathion-LA	291	27.93	1.005	L	2	A B
111	T	Ethion-L	231	32.25	1.160	L	2	A B
112	I	Pyrene-d10-LS	212	30.00	1.000	L	1	A B
113	T	Fluoranthene-L	202	29.23	0.974	L	2	A B
114	T	Pyrene-LA	202	30.06	1.002	L	2	A B
115	T	Retene-L	219	31.49	1.050	L	2	A B
116	I	p,p'-DDE-d8-LS	326	30.84	1.000	L	1	A B
117	T	o,p'-DDE-L	318	29.86	0.968	L	2	A B
118	T	p,p'-DDE-LA	318	30.90	1.002	L	2	A B
119	T	o,p'-DDD-L	235	31.09	1.008	L	2	A B
120	T	p,p'-DDD-L	235	32.21	1.044	L	2	A B
121	I	p,p'-DDT-d8-LS	243	33.31	1.000	L	1	A B
122	T	o,p'-DDT-L	235	32.21	0.967	L	2	A B
123	T	p,p'-DDT-LA	235	33.38	1.002	L	2	A B
124	T	Methoxychlor-L	227	35.11	1.054	L	1	A B
125	I	Triphenylene-d12-LS	240	34.84	1.000	L	1	A B
126	T	Benzo(a)anthracene-L	228	34.87	1.001	L	2	A B
127	T	Chrys-L +Triph-LA	228	34.99	1.004	L	2	A B
128	I	Benzo(a)pyrene-d12-LS	264	39.79	1.000	L	1	A B
129	T	Benzo(b)fluoranthene-L	252	38.90	0.978	L	2	A B
130	T	Benzo(k)fluoranthene-L	252	38.90	0.978	L	2	A B
131	T	Benzo(e)pyrene-L	252	39.69	0.998	L	2	A B
132	T	Benzo(a)pyrene-LA	252	39.86	1.002	L	2	A B

133	I	Benzo(ghi)perylene-d12-LS	288	44.19	1.000	L	1	A	B
134	T	Indeno(1,2,3-cd)pyrene-L	276	43.41	0.982	L	2	A	B
135	T	Dibenz(a,h)anthracene-L	278	43.57	0.986	L	2	A	B
136	T	Benzo(ghi)perylene-LA	276	44.29	1.002	L	2	A	B

Cal A = Average L = Linear LO = Linear w/origin Q = Quad QO = Quad w/origin
#Qual = number of qualifiers
A/H = Area or Height
ID R = R.T. B = R.T. & Q Q = Qvalue L = Largest A = All

Standard Operating Procedure for GC/MS NCI Sample Analysis

Simonich Environmental Chemistry Laboratory
1161 Ag and Life Sciences Building
Dept. of Environmental & Molecular Toxicology
Oregon State University
Corvallis, OR 97331-7304

Prepared by Glenn Wilson
Version 1.1
January 2004

Standard Operating Procedure for
GC/MS NCI Sample Analysis

Approvals:

Staci Simonich
Oregon State University
Principal Investigator

Staci I. Simonich 10/7/04
Signature *Date*

Dave Schmedding
Senior Research Assistant

10/11/04
Signature *Date*

Glenn Wilson
Research Assistant

Glenn Wilson 10-11-04
Signature *Date*

Standard Operating Procedure for GC/MS NCI Sample Analysis

Table of Contents:

1.0 Scope and Application

1.1 This method details the procedure for analysis of samples using the gas chromatograph/mass spectrometer negative chemical ionization (GC/MS NCI) instrument. This instrument is an Agilent 5973 MSD equipped with a J&W 30 meter x .25mm x .25um DB5-MS column.

2.0 Summary of Method

2.1 This check assumes the GC/MS is within normal operational parameters. Also assumed is that the operator is familiar with the operation of the instrument. First, decafluorotriphenylphosphine (DFTPP) is injected as a quick test for instrument operation and sensitivity. Secondly, a daily standard is run to ensure the fitness of the instrument for the analysis being performed. Lastly, the samples will be run.

3.0 Run and evaluate DFTPP

3.1 Make sure the solvent rinse vials in the autosampler turret are filled. The "solvent a" should be acetone, and "solvent b" and "solvent b2" should be dichloromethane (DCM).

3.2 Raise the GC column oven temperature to about 300 degrees C if it has not been used recently.

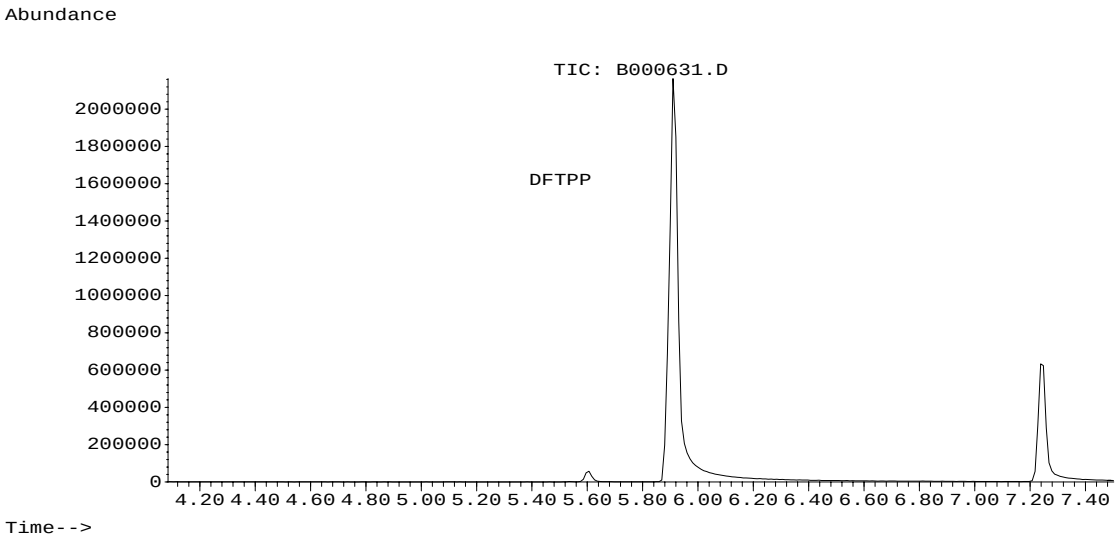
3.3 Turn the methane flow up to 40 and let flow for about ½ hour.

3.4 Make a run sequence and run the standard. Be sure to fill out the instrument run logbook. The standard aliquot concentration should be 1 ng/µl. The current run method is DFT02_N.

3.5 Evaluate the run when it is finished. The peak height should be over million counts. The degradation (later) peak should be less than 25% of the main (first) peak. The baseline should be relatively low and clean. If these conditions are not met, rerun the DFTPP aliquot. If the second run does not appear to be good, try to determine the origin of the problem. . A poor run may be due to earlier runs of dirty samples, old standards, incorrect solvents, or a corrupted run method. Seek help if the problem is not resolved. Changing an injection liner or clipping the column may be required to obtain satisfactory instrument performance.

3.6 When the DFTPP run is judged to be satisfactory, proceed to running a standard.

3.7 See Section 9.0 for the DFTPP GC/MS run parameters.



4.0 Run and evaluate a target SOC standard

4.1 Make sure the solvent rinse vials in the autosampler turret are filled. The "solvent a" should be acetone, and "solvent b" and "solvent b2" should be compatible with the solvent used in the standard to be run.

4.2 Make a run sequence and run the standard. Be sure to fill out the instrument run logbook. The sample aliquot should be either a midpoint in the calibration curve, or a daily control standard generated with the sample to be run. The SIM method is OC02S_N. See Section 10.0 for the method parameters. Table 1 lists the SOCs that are analyzed by negative chemical ionization.

4.3 When the run is completed, quant and Qedit the run. Pay attention to retention times, spectral data and other qualifying information to determine correct compound identification. (what limits do we need for recoveries?) Be sure all compounds are present. There may be a need to adjust SIM windows if the column has been cut. Some compounds may be seen only partially if window assignments are incorrect. If this is so, run the standard on the full scan acquisition method so that window assignments may be evaluated. The full scan method is OC02_N. See appendix C for the method parameters.

4.4 Rerun and evaluate the daily standard with the SIMS method if adjustments were made to window times.

Table 1. SOCs Analyzed by Negative Chemical Ionization

PCBs: PCB 52 (2,2',5,5'-Tetrachlorobiphenyl), PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl) Pesticides and degradation products: Hexachlorocyclohexanes (HCH) - α*, β, γ-(lindane), and δ, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlor Epoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex Polybrominated Diphenyl Ethers Surrogates: $^{13}C_{12}$ PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), $^{13}C_{12}$ PCB 180 (2,2', 3,4,4',5,5'-Heptachlorobiphenyl), d_{10} - Chlorpyrifos, $^{13}C_6$-HCB, d_6-γ-HCH, d_4-Endosulfan I, d_4-Endosulfan II Internal Standards: d_{14}-Trifluralin

5.0 Run the Samples

5.1 Evaluate the samples to determine if they need pre-screening on the gas chromatograph/flame ionization detector (GC/FID). For example, samples that are very viscous or highly colored would be pre-screened on the GC/FID.

5.2 Make a sequence and run the samples using the SIMS method OC02S_N.

6.0 GC/MS Data Analysis

6.1 Overview- The sample data is loaded, the appropriate method is loaded, and the sample is quantified using a calibration previously established. After quantification, the sample is edited to ensure quality. The following section goes

through the steps used in this process. The **bold** indicates the menu choice which is left clicked with the mouse.

6.2 Loading the data file- Select **View, Data Analysis, File, Load Data File**.

6.3 Loading the method- Select **File, Load Method,(Method Name)**

6.4 To quantify- Select **Quant, Calculate**.

6.5 To edit- Select **Quant, Qedit**.

7.0 Pollution Prevention

7.1 The chemicals used in this method pose little threat to the environment.

7.2 For further information on pollution prevention consult *Less is better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington D.C. 20036, (202) 872-4477.

8.0 Waste Management

8.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

8.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington DC, 20036.

9.0 GC/EI-MS parameters for DFTPP analysis

INSTRUMENT CONTROL PARAMETERS

Sample Inlet: GC
Injection Source: GC ALS
Mass Spectrometer: Enabled

==========
6890 GC METHOD
==========

OVEN
Initial temp: 150 'C (On) Maximum temp: 325 'C
Initial time: 1.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	20.00	240	2.00
2	20.00	320	4.00
3	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 15.50 min

FRONT INLET (UNKNOWN) BACK INLET ()
Mode: Pulsed Splitless
Initial temp: 280 'C (On)
Pressure: 13.66 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 0.50 min
Purge flow: 20.0 mL/min
Purge time: 0.40 min
Total flow: 24.1 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 2.00 min
Gas type: Helium

COLUMN 1 COLUMN 2
Capillary Column (not installed)
Model Number: Agilent 122-5532
DB-5ms, 0.25mm * 30m * 0.25um

Max temperature: 350 'C
Nominal length: 29.9 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 13.66 psi
Average velocity: 39 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET) BACK DETECTOR (NO DET)

SIGNAL 1
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 2
Use: MSD Transfer Line Heater
Description: TransferLine
Initial temp: 280 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector

Front Injector:

Sample Washes 1
Sample Pumps 4
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 2
PostInj Solvent B Washes 2
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:
No parameters specified

MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File : NCI06.U
Acquistion Mode : Scan

MS Information
-- -----------

Solvent Delay : 4.00 min

EM Absolute : True
Resulting EM Voltage : 1905.9

[Scan Parameters]

Low Mass : 45.0
High Mass : 500.0
Threshold : 100
Sample # : 3 A/D Samples 8
Plot 2 low mass : 40.0
Plot 2 high mass : 510.0

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 150 C maximum 300 C

10.0 GC/EI-MS parameters for target SOC analysis

INSTRUMENT CONTROL PARAMETERS

Sample Inlet: GC
Injection Source: GC ALS
Mass Spectrometer: Enabled

==========
6890 GC METHOD
==========

OVEN
Initial temp: 60 'C (On) Maximum temp: 325 'C
Initial time: 1.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	6.00	300	3.00
2	20.00	320	9.00
3	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 54.00 min

FRONT INLET (UNKNOWN) BACK INLET ()
Mode: Pulsed Splitless
Initial temp: 300 'C (On)
Pressure: 8.33 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 0.60 min
Purge flow: 20.0 mL/min
Purge time: 0.50 min
Total flow: 24.1 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 1.00 min
Gas type: Helium

COLUMN 1 COLUMN 2
Capillary Column (not installed)
Model Number: Agilent 122-5532
DB-5ms, 0.25mm * 30m * 0.25um
Max temperature: 350 'C
Nominal length: 29.9 m

Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 8.44 psi
Average velocity: 37 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET) BACK DETECTOR (NO DET)

SIGNAL 1
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 2
Use: MSD Transfer Line Heater
Description: TranferLine
Initial temp: 300 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes 1
Sample Pumps 4

Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 2
PostInj Solvent B Washes 2
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:
No parameters specified

MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File : NCI06.U
Acquistion Mode : SIM

MS Information
-- -----------

Solvent Delay : 10.00 min

EM Absolute : True
Resulting EM Voltage : 1905.9

[Sim Parameters]

GROUP 1
Group ID : Trifluralin
Resolution : Low
Plot 1 Ion : 305.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(305.1, 20) (319.2, 20) (335.1, 20)
(336.1, 20) (349.2, 20) (350.2, 20)

GROUP 2
Group ID : HCH
Resolution : Low
Group Start Time : 21.30
Plot 1 Ion : 252.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(70.0, 20) (71.0, 20) (72.0, 20)
(73.0, 20) (74.0, 20) (252.9, 20)
(262.9, 20) (281.8, 20) (283.8, 20)
(285.8, 20) (289.8, 20) (291.8, 20)
(293.8, 20)

GROUP 3
Group ID : Chlorothalonil
Resolution : Low
Group Start Time : 23.20
Plot 1 Ion : 160.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(71.0, 40) (160.1, 40) (161.1, 40)
(253.0, 40) (255.0, 40) (263.9, 40)
(265.9, 40) (267.9, 40)

GROUP 4
Group ID : Metribuzin
Resolution : Low
Group Start Time : 24.70
Plot 1 Ion : 184.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(184.1, 40) (198.1, 40) (199.1, 40)
(265.9, 40) (267.9, 40) (299.9, 40)

GROUP 5
Group ID : Chlorpyrifos
Resolution : Low
Group Start Time : 26.05
Plot 1 Ion : 214.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(214.0, 20) (237.0, 20) (239.0, 20)
(255.0, 20) (292.0, 20) (294.0, 20)
(297.0, 20) (298.0, 20) (299.0, 20)
(313.0, 20) (315.0, 20) (322.0, 20)
(324.0, 20) (329.9, 20) (331.9, 20)
(333.9, 20)

GROUP 6
Group ID : Hep Epox
Resolution : Low
Group Start Time : 27.50
Plot 1 Ion : 289.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(289.9, 20) (291.9, 20) (293.9, 20)

(351.9, 20) (387.8, 20) (389.8, 20)
(391.8, 20) (407.9, 20) (409.9, 20)
(411.9, 20) (413.9, 20) (423.9, 20)
(425.9, 20)

GROUP 7
Group ID : Endo I
Resolution : Low
Group Start Time : 28.30
Plot 1 Ion : 323.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(263.9, 20) (265.9, 20) (267.9, 20)
(323.9, 20) (325.9, 20) (327.9, 20)
(335.9, 20) (337.9, 20) (339.9, 20)
(369.9, 20) (371.9, 20) (373.9, 20)
(375.9, 20) (377.9, 20) (403.9, 20)
(407.9, 20) (409.9, 20) (411.9, 20)
(441.9, 20) (443.9, 20) (445.9, 20)

GROUP 8
Group ID : Dieldrin
Resolution : Low
Group Start Time : 29.55
Plot 1 Ion : 345.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(296.0, 40) (298.0, 40) (300.0, 40)
(345.9, 40) (347.9, 40) (379.9, 40)

GROUP 9
Group ID : Endo II
Resolution : Low
Group Start Time : 30.50
Plot 1 Ion : 323.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(323.9, 30) (325.9, 30) (327.9, 30)
(371.9, 30) (405.9, 30) (407.9, 30)
(409.9, 30) (411.9, 30) (413.9, 30)
(441.8, 30) (443.8, 30) (445.8, 30)

GROUP 10
Group ID : Endrin ald
Resolution : Low
Group Start Time : 31.00
Plot 1 Ion : 345.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(345.9, 40) (358.0, 40) (360.0, 40)
(362.0, 40) (379.9, 40) (381.9, 40)

GROUP 11
Group ID : Endo Sulfate
Resolution : Low
Group Start Time : 31.75
Plot 1 Ion : 357.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(357.9, 40) (359.9, 40) (361.9, 40)
(385.9, 40) (387.9, 40) (421.9, 40)

GROUP 12
Group ID : Hepta PCB
Resolution : Low
Group Start Time : 32.35
Plot 1 Ion : 393.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(367.8, 30) (369.8, 30) (393.9, 30)
(395.9, 30) (397.9, 30) (403.8, 30)
(405.9, 30) (407.9, 30) (409.9, 30)

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 150 C maximum 300 C

Compound List Report MSD B

Method : C:\MSDCHEM\1\METHODS\02SA01_N.M (RTE Integrator)
Title : Calibration curve 10-20-03
Last Update : Mon Dec 22 08:06:40 2003
Response via : Initial Calibration
Total Cpnds : 53

PK#		Compound Name	QIon	Exp_RT	Rel_RT	Cal	#Qual	A/H	ID
1	I	d6-HCH, alpha-IS	72	21.42	1.000	A	2	A	B
2	S	d14-Trifluralin	349	20.84	0.973	A	2	A	B
3	S	13C-HCB	292	21.63	1.009	A	2	A	B
4	S	d6-HCH, gamma	72	22.61	1.055	A	2	A	B
5	S	d10-Chlorpyrifos	322	26.21	1.223	A	2	A	B
6	I	d6-PCB 77-IS	298	29.80	1.000	A	2	A	B
7	S	d4-Endosulfan I	378	28.71	0.964	A	2	A	B

8	S	13C-PCB 101	338	28.63	0.961	A	2	A	B
9	S	d4-Endosulfan II	412	30.61	1.027	A	2	A	B
10	S	13C-PCB 180	406	34.01	1.141	A	2	A	B
11	I	d14-Trifluralin-LS	349	20.84	1.000	A	2	A	B
12	T	Trifluralin	335	21.00	1.008	A	2	A	B
13	I	13C6-HCB-LS	292	21.63	1.000	A	2	A	B
14	T	Hexachlorobenzene	284	21.63	1.000	A	2	A	B
15	T	Chlorothalonil	266	23.46	1.085	A	2	A	B
16	T	Heptachlor	266	25.17	1.164	A	2	A	B
17	T	Dacthal	332	26.46	1.224	A	2	A	B
18	I	d6-gamma-HCH-LS	72	22.61	1.000	A	2	A	B
19	T	HCH, alpha	71	21.57	0.954	A	2	A	B
20	T	HCH, beta	71	22.61	1.000	A	2	A	B
21	T	HCH, gamma (Lindane)	71	22.75	1.006	A	2	A	B
22	T	HCH, delta	71	23.88	1.056	A	2	A	B
23	T	Triallate	160	23.80	1.053	A	1	A	B
24	T	Metribuzin	198	24.85	1.099	A	2	A	B
25	T	Aldrin	237	26.33	1.164	A	2	A	B
26	I	d10-Chlorpyrifos-LS	322	26.21	1.000	A	2	A	B
27	T	Chlorpyrifos oxon	297	26.18	0.999	A	2	A	B
28	T	Chlorpyrifos	313	26.34	1.005	A	2	A	B
29	I	d4-Endosulfan I-LS	378	28.71	1.000	A	2	A	B
30	T	Heptachlor epoxide	390	27.62	0.962	A	2	A	B
31	T	Chlordane, oxy	424	27.61	0.962	A	2	A	B
32	T	Chlordane, trans	410	28.39	0.989	A	2	A	B
33	T	Endosulfan I	404	28.79	1.003	A	2	A	B
34	T	Chlordane, cis	266	28.79	1.002	A	2	A	B
35	T	Nonachlor, trans	444	28.88	1.006	A	2	A	B
36	T	Dieldrin	346	29.64	1.032	A	2	A	B
37	I	13C-PCB 101-LS	338	28.63	1.000	A	2	A	B
38	T	PCB 52 (tetra)	292	26.34	0.920	A	2	A	B
39	T	PCB 74 (tetra)	292	27.69	0.967	A	2	A	B
40	T	PCB 101 (penta)	326	28.63	1.000	A	2	A	B
41	T	PCB 118 (penta)	326	30.57	1.068	A	2	A	B
42	I	d4-Endosulfan II-LS	412	30.61	1.000	A	2	A	B
43	T	Endrin	346	30.29	0.990	A	2	A	B
44	T	Endosulfan II	406	30.67	1.002	A	2	A	B
45	T	Nonachlor, cis	444	30.80	1.006	A	2	A	B

46	T	Endrin aldehyde	380	31.13	1.017	A	2	A	B
47	T	Endosulfan sulfate	386	31.87	1.041	A	2	A	B
48	I	13C-PCB 180-LS	406	34.01	1.000	A	2	A	B
49	T	PCB 153 (hexa)	360	31.22	0.918	A	2	A	B
50	T	PCB 138 (hexa)	360	32.03	0.942	A	2	A	B
51	T	PCB 187 (hepta)	394	32.45	0.954	A	2	A	B
52	T	PCB 183 (hepta)	394	32.62	0.959	A	2	A	B
53	T	Mirex	368	35.14	1.033	A	2	A	B

Cal A = Average L = Linear LO = Linear w/origin Q = Quad QO = Quad w/origin
#Qual = number of qualifiers
A/H = Area or Height
ID R = R.T. B = R.T. & Q Q = Qvalue L = Largest A = All

APPENDIX B

Laboratory Quality Assurance Manual

Trace Element Environmental Analytical Chemistry Project

U.S. Geological Survey
National Research Program
Boulder, Colorado

Revised April 2003

Table of Contents

1. Definition, Purpose, and Scope

Definition of Terms

Quality Assurance Program: An orderly assemblage of management policies, objectives, principles, and general procedures by which a laboratory outlines how it intends to produce data of known and accepted quality.

Quality Assurance: The total integrated program for assuring the reliability of monitoring and measurement data. A system for integrating the quality planning, quality assessment, and quality improvement efforts to meet user requirements.

Quality Control: The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurements process.

Quality Assessment: The overall system of activities to provide assurance that the QC task is being performed effectively. Quality Assessment involves a continuing evaluation of performance of the production system and the results produced.

Standard Operating Procedure: A detailed written procedure designed to systematize and standardize the performance of the procedure.

Purpose of Manual

The purpose of this manual is to describe the QA/QC Program for all laboratory practices in order to generate the most precise and accurate data possible. To achieve this purpose, a comprehensive and scientifically sound QA Plan has been implemented and is now used.

Scope – Objectives

The ultimate goal of the laboratory is to produce quality data that is accurate, precise, complete, representative, and compatible. While proper validated methodologies are necessary, these alone are not sufficient to assure data quality. The QA Plan is designed to control and monitor laboratory activities, ensuring the laboratory meets the data quality objectives listed above. During the course of generating data on samples for inorganic parameters, it is the policy of the Project to 1) apply the best laboratory practices 2) use approved methodology when mandated by regulation and use standardized methodology, if possible 3) when approved methodology is not applicable, fully document all operations associated with the generation of data and 4) meet certain quality requirements that will be designated in the following paragraphs. It should be noted, however, that occasionally certain matrices and samples present analytical challenges, or are not amenable to standardized methodology. In these instances modifications to standard protocols may have to be made to produce a high quality analysis. When this occurs, any deviations from standard operating procedures will be documented.

This QA Program will be carried out under the direction of the Project Chief. It covers all aspects of sample receiving, storage, preparation, analysis, and reporting. Standard QC procedures, data reduction, and reporting will be in compliance with requirements in *Standard Methods for Examination of Water and Wastewater*, 19th ed. or later editions. Written methods for sample receipt, chain of custody, preservation, storage, preparation, analysis, safety, and reporting shall be followed. Log books, printed documents, data, or other written documentation shall be available to describe the work performed in each of the following stages of analysis:

- Chain of custody
- Sample preservation
- Sample receipt
- Sample storage
- Sample preparation
- Sample analysis
- Data reduction
- Data reporting
- QA/QC

2. Organization and Responsibility

Executing an effective QA program in the laboratory demands the commitment and attention of both management and staff. All laboratory personnel within the organization play a vital role in assuring a continued commitment to the quality of work accomplished. (See Figure 1, Project Organizational Chart). The laboratory staff is highly qualified and trained in the following areas:

- Trace element analysis
- Ion chromatography (IC)
- Analytical methods development
- Inductively coupled plasma-atomic emission spectrometry
- Inductively coupled plasma-mass spectrometry
- Cold vapor atomic fluorescence spectrometry

Project Chief

The Project Chief is responsible for all operational activities within the laboratory and is accountable for all data generated by the laboratory. QA responsibilities consist of:

- Final review of all data generated by the laboratory
- Final authority to release data to requestor
- Final authority on all analytical procedures and SOPs used by laboratory personnel
- Coordinates with Project Staff in implementing the laboratory QA plan and its policies, revisions, and any corrective action to ensure compliance.
- Periodic audits of the QA Plan to ensure the objectives and procedures are being followed

Laboratory Staff

Since the greatest amount of responsibility for a successful QA Program rests with the analysts, it is important that they be highly qualified and competent. New and experienced laboratory personnel shall be carefully trained for new specific work assignments. Laboratory personnel have onsite access to technical journals and textbooks as well as access to the University of Colorado library. Combined administrative and technical staff meetings will be held to help provide a good information exchange forum. Laboratory personnel are responsible for:

- Having a working knowledge of the QA Plan

- Ensuring that all work generated is in compliance with QC acceptance criteria
- Performing all work according to a written methods or new research methods
- Ensuring that all documentation to their work is complete and accurate
- Ensuring that acceptance of any data outside QC criteria must be approved by laboratory management
- Maintaining records for all QC data
- Notifying management immediately of any QC issues
- Writing and updating SOPs or documentation of research methods
- Meeting sample holding and turnaround times
- Reviews all analysis report forms for completeness
- Reviews all analysis request forms to ensure compliance within contractual obligations
- Ensures requestor receives the final completed data report
- Maintains records and archives of all data reports and working data files

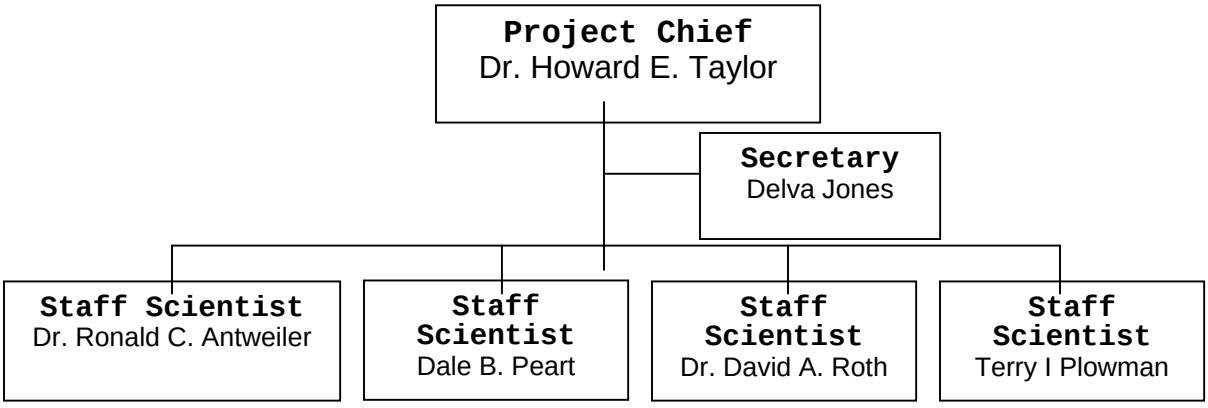


Figure 1. Project Organization Chart

3. Sampling Procedures

Sample Containers and Holding Times

Where appropriate, the laboratory supplies all necessary sampling materials for field sampling activities. Using properly cleaned containers and correct preservatives as well as adhering to proper holding times are essential factors for maintaining sample integrity and representativeness. Requirements for sample containers, preservation techniques, and holding times are found in one of the following references (or later editions):

- *Standard Methods for the Examination of Water and Waste Water*, American Public Health Association, et al., 19th Edition, or later
- *Federal Register* Volume 49, No. 209, Friday, October 26, 1984, EPA, 40 Code of Federal Regulations, Part 136
- *Handbook for Sampling and Sample Preservation of Water and Wastewater*, EPA 600/4-82-029, September 1982. Methods for cleaning and preparing glassware and sample containers are strictly complied with to ensure that the sample is not contaminated during the collection process due to containers. Appropriate volumes of the sample must also be collected to ensure that the required detection limits can be met, the QC samples analyzed, and any necessary sample reanalysis performed.
- *Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments*, *U.S. Geological Survey, Techniques for Water Resources Investigations,* USGS, Book 5, Washington, D.C. (1985).
- Published procedures or project proposals

Sample Submittal

Samples are brought to the laboratory by delivery services or field sampling crews. Any sample taken in a nonstandard container, improperly preserved, or shipped in an unacceptable manner may be rejected. Each sample or group of samples needs to be entered into the Field and Laboratory Database System. This can be done either manually in the laboratory or in the field and then electronically transferred directly into database. All pertinent data is tracked by the Database System, such as the date, time, location, field sampler, field data, laboratory tests requested, etc

Sample Storage and Handling

The samples received by the laboratory are placed in appropriate storage or sent directly to the test area. The storage areas are located in the laboratory and consist of refrigerators at 4ºC, freezers at -10ºC, and designated storage cabinets for sample types, (i.e., metals, standard minerals, etc.). Once the analysis is completed, the remaining sample is kept an additional 30-60 days in storage, then discarded. If a the sample submitter should request return of a sample prior to the expiration interval, it will be returned in a manner that meets the required criteria.

Quality Assurance Sample

To evaluate and ensure acceptable results, the laboratory requires that samplers submit with their samples travel blanks, field blanks, and/or duplicate samples. For specific requirements, see published procedures.

4. Sample Custody Procedures

When appropriate, a Chain of Custody form must be completed for samples received by the laboratory which may be used as evidence for enforcement purposes. Once a sample is received, the Chain of Custody Officer or the alternate is notified. All information is then transcribed to the Chain of Custody form and the sampler signs the form, witnessed by the Chain of Custody Officer or alternate. The sample is then transferred to the appropriate location to wait for analysis. For each transfer of physical custody, an entry of disposition and one of receipt is made on the custody form.

While in the laboratory, samples are stored in secure areas under appropriate preservation and environmental conditions. Following the completion of the analysis, the samples are stored until the results are submitted to the Program Manager and permission to discard has been received. A notation of completion is made on the Chain of Custody form, and the document is then filed with the analysis report. Copies of the files are maintained in project archives.

5. Calibration and Measurement Procedures

Calibration of instruments is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet required detection limits. In general, calibration is accomplished by measuring instrument response to standards containing the analytes in known

concentrations while being in compliance with manufacturer's recommendations.

Instrument Calibration and Frequency

Today’s complex instrumentation and calibration frequencies are extremely varied; therefore, a bound notebook is assigned to each instrument to log the following:

- All maintenance performed
- All daily sensitivity checks and/or calibration results where applicable according to published methodology
- All manufacturer's maintenance and repairs
- Each log entry will contain the date, operator's name, and operation performed (i.e., maintenance, sensitivity check, etc.).
- Calibration is accomplished on a daily basis or whenever the following instruments are used:
- Atomic Fluorescence Spectrometers
- Spectrophotometers
- Ion Chromatographs
- Inductively Coupled Plasma-Atomic Emission Spectrometers
- Inductively Coupled Plasma-Mass Spectrometers
- Auto Titrators
- Auto Analyzers

Other instruments may require weekly, monthly, quarterly, or even semiannual calibration (i.e., balances, ovens, exhaust hoods, etc.).

For analytical instrument calibration, once a standard calibration range has been established, at least five standards are normally used in daily standardization where applicable. For specifics, see the SOP or published methods for a particular analytical procedure. If a problem arises which cannot be corrected by the instrument operator, then the instrument specialist is notified. The officer will coordinate the necessary diagnostic and corrective measures to be implemented. Documentation will be provided in the instrument log book.

Calibration Standards/Reagents Preparation

A critical area in the generation of quality data is the quality, purity, and traceability of the standards and reagents used in analytical calibration procedures. All primary reference standards and standard solutions used by the laboratory are obtained from the National Institute of Standards and Technology or commercial manufacturers. All standards, standard solutions, and reagents are validated prior to being used. Validation procedures range from a check for purity to verification of concentration of the standard using standards prepared at a

different time or from a different source. All Stock Standards are labeled as to the following:

- Name and Concentration of Stock
- Method of Preparation
- Date Prepared/Preparer's Name
- Supplier, Purity, Lot Number, and Expiration Date
- Any other pertinent information

New working standards are compared to the remainder of the current working standards for any concentration differences, formation of precipitates, and any signs of deterioration. Reagents are also examined for purity by subjecting an aliquot to the analytical method for its intended use. For example, reagent water, acids, or preservatives are analyzed for possible contamination prior to use.

Water used to prepare calibration standards, spike solutions, standard reference solutions or any sample dilutions or mixtures must meet or exceed the requirements for Type I grade water as specified by the American Society for Testing and Materials (ASTM); Standard Practice D 1193. This grade water is equivalent to Type I water as specified in Standard Methods 1080. The parameter measured to verify the quality of water is resistivity, with a requirement of 18 megohm-cm at 25°C or better. See also section 2.2 of "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," (EPA 600/4-79-019, March l979), and any future updates of the manual.

Reagents must be ACS reagent grade quality or better. Reagents and standards will be dated upon receipt and will be properly disposed of when the shelf life has been reached. Working solutions and mixtures made from stock reagents and standards will be used only for the appropriate working life of the solution. In general, this is from one week to no more than six months for materials that tend to degrade. In the absence of specific guidelines for working reagents and standards, the primary analyst may choose to prepare these materials fresh each time the analysis is performed or use the sample holding times as a guide for the useful working life. For other materials that do not degrade easily (e.g., simple salts, solutions for metals analyses) the shelf life may be much longer.

6. Analytical Procedures

Analytical methods are derived from the latest editions of the following references:

- *Methods for Chemical Analyses of Water and Wastes*, EPA-600/4-79-020 (revised March 1983
- *Standard Methods for the Examination of Water and Wastewater*, 19th Edition or later, APHA, American

Water Works Association, Water Pollution Control Federation, Washington, D.C. (1992)

- *Methods for Determination of Inorganic Substances in Water and Fluvial Se*diments, Techniques of Water Resources Investigations, USGS, Book 5, Washington, D.C. (1985)

- *Annual Book of American Society for Testing and Materials Standards*, Volumes 11.01 and 11.02, ASTM, Philadelphia, Pennsylvania (1988)

- *Official Methods of Analysis*, 14th Edition, AOAC International, Arlington, Virginia (1984)

The following are typical methods for trace metal analysis of various types of samples. These are not to be construed as being complete or the only methods to be used for the specified sample types:

Water. Monitoring well, ambient water, effluents, and other water samples are analyzed by ICP-AES or ICP-MS according to methods Garbarino and Taylor (1979), Mitko and Bebek, (1999, 2000), Garbarino and Taylor, (1995), and Taylor, (2001). Where the detection/quantitation technique is specified by program requirements. Mercury analyses are performed according to cold vapor atomic fluorescence spectrometric methods (Roth, 1994; Roth and others, 2001).

Soil and Sediment A 50 g aliquot (approximately) is taken from a well mixed
sample and weighed in a precleaned dish. The sample is either freeze-dried or subsampled wet (requiring a moisture determination to report on a dried basis). The dried sample is ground to fineness and 0.1 g of subsample is taken for analysis. Sample digestion is conducted with a mixture of mineral acids in a closed-system microwave digestion oven, as reported by Hayes et.al. (1993). Initial weights and final volumes may be adjusted depending on expected sample concentrations and detection level requirements. Trace metals analyses are performed as specified above.

Fish Whole fish or specified dissected organs are initially prepared by homogenization followed by freeze-drying and a closed system nitric acid digestion using a microwave oven. Trace metals analyses are performed as specified above.

Meat Other tissues are prepared and analyzed the same as fish tissue. New matrices will be observed closely as an additional precaution to ensure proper digestion. If a new matrix does not respond favorably to the digestion, additional methods development may be required.

Vegetation Plant tissues are prepared and analyzed in a similar manner to the fish tissue. New matrices will be observed closely as an additional precaution to ensure proper digestion. If a new matrix does not respond favorably to the digestion, additional methods development may be required.

Standard Operating Procedure

Analytical methods chosen are dependent upon certain objectives, some of which consist of precision and accuracy, type of sample matrix, and quantitative sensitivity. Each analytical method routinely used is documented in the form of a SOP which contains complete detailed instructions to standardize the expected performance of the analytical method. In the absence of a method, validated research methods are used for custom analyses. Occasionally, the primary analyst will encounter a situation that is not addressed by available guidelines. The analyst should consult the Project Chief in these cases. When possible, decisions will be based on the data quality objectives of the project. For example, if while performing triplicate analyses one result is above the PQL and the other two are below (but above the MDL), it may be determined that the PQL is well below the regulatory level or study level of concern and thus the average of the three results will be reported. If study requirements determine that results at the PQL are of importance, the primary analyst may be required to rerun the analyses to clarify or confirm the results.

Analytical Methodology Verification

Before any analytical method is routinely used to generate data, the method is validated. Criteria used to validate a method consist of the following:

- Method selection by senior staff
- Testing of method verifying reporting limits, dynamic range, matrix effects, precision, and accuracy criteria
- Data acceptance criteria must be approved by the Project Chief
- Final documentation of the method in a written SOP or published report

7. Data Reduction, Validation, and Reporting

The final step in analyzing samples is to review the data collected prior to reporting. The analytical data generated within the laboratory are extensively checked and crosschecked for their accuracy, precision, and completeness. The validation process consists of data generation, reduction review, and finally reporting results to the submitter.
The primary responsibility for the generation of accurate data rests with the analyst. The analyst performs the data calculation functions and is responsible for the initial examination of the finished data. All data reduction steps applied to the raw data are outlined in the appropriate analytical SOPs. Each analyst reviews the quality of their work based on the following guidelines:

- The appropriate method has been followed

- Sample preparation is correct and complete
- Analytical results are correct and complete
- Blank correction procedures are followed, if applicable
- QC samples are within established QC limits
- All documentation is complete, including analysis report, QC form, and QC charts

The QC procedures outlined in the analytical SOP are used for the preliminary validation of the results along with any historical data, if available. When applicable, correlation checks are used to validate the data, such as anion-cation balances, specific conductance versus dissolved solids, dissolved solids versus calculated dissolved solids, After data reduction and validation steps are computed, the analyst enters the data into the Database System and releases the QC batch. The data package is then forwarded electronically in the Database to the appropriate staff scientist, who evaluates the data along with all pertinent QC results such as laboratory control standards, matrix spikes, surrogates, duplicates, blind duplicates, blind performance evaluation samples, and laboratory performance records, as well as historical records to help form a basis for acceptance of data. If the data package passes QA/QC criteria, it is released in the Database System to the senior staff. A data package containing the required QC batches for each sample submittal is then reviewed by senior staff for final validation, completeness, and acceptance. The final review is based on the following criteria:

- Calibration data reviewed
- Appropriate methodologies used
- QC samples within established guidelines
- Comparison of historical data when available
- Correlation checks reviewed (i.e., anion-cation
- balance, electrical conductivity versus total dissolved solids, etc., when applicable
- Evaluation of data in general by comparability, assessment, and reasonableness of sample types, (i.e., wastewaters, surface waters, groundwaters, etc.)
- Ensures completion of all analytical work requested

After validation and review by senior staff, the approved data package is incorporated into a final analysis report. The final report is released to the submitter either in a printed format with all the appropriate information or sent to the submitter in electronic format. The full data package is then archived for possible future use. Errors or problems which may occur are documented and transmitted to the appropriate section. The cause of the errors is then addressed either by further training or reevaluation of the analytical method to ensure quality data are generated at the analyst level.

8. Internal Quality Control Checks

Internal QC is the routine activities and checks such as calibrations, replicate analysis, spiked samples, etc. included in normal procedures to control accuracy and precision of the measurement process. It determines whether the laboratory operations are within acceptable QC guidelines during data generation.

Blanks

Field Blanks are check samples which monitor contamination originating from the collection, transport, and storage of environmental samples. Laboratory prepared blank water is supplied to field personnel for processing in the same manner as samples; this includes field filtration and addition of preservatives.

Travel Blanks are prepared in the laboratory from ultrapure water. When appropriate, they are supplied to field personnel with each batch of empty sample bottles and are returned with the collected samples.

Method Blanks are prepared from laboratory blank water, substituted for samples, and analyzed with every sample set. Method blanks are used to determine the level of contamination that exists in the analytical procedure. Contamination may or may not lead to elevated concentration levels or false positive data. Ideally, the concentration of an analyte in the method blank is below the method detection level for the analyte. However, for some analytical methods, elimination of blank contamination is extremely difficult; therefore, each analytical SOP has a method blank level of acceptance. If the acceptance contamination level is exceeded, the sample set is reanalyzed.

Reagent Blank is the concentration of analytes in the preservation reagents or reagents used for chemical processing during analysis, such as digestions. Reagent blanks are subtracted from the analysis result where appropriate. A minimum of 10 % reagent blanks will be measured during any given sample run.

Calibration Standards

Calibration standards are routinely run with every sample set. Calibration standards must fall within certain QC limits before any sample results can be accepted. The limits are found in the particular analytical method being used. If the calibration standards are unacceptable, the sample results are rejected, corrective action taken, and the samples reanalyzed. A correlation coefficient (r) of 0.995 or greater is acceptable for calibration curves. If this criterion is not met, the curve must be repeated. If the criterion is again not met, the primary analyst must find the source of the problem before proceeding with analyses.

Check Standards

The check standard is usually a midrange calibration standard used to monitor the analytical method. The check standard is analyzed every ten samples to provide evidence that the laboratory is performing the method within accepted QC guidelines. As long as check standard results fall within established control limits, the analysis can continue. If check standard results fall outside the control limits, the data are suspect and the procedure is stopped. The analytical procedure is checked for error step by step by the analyst. Once the procedure is again acceptable, reanalysis of samples begins with the last check standard that was within acceptable control limits.

Laboratory Control Sample (Standard Reference Samples)

Laboratory control samples are analyzed routinely to verify the analytical method is in control and to also serve as a second source verification for the calibration standards of all routine analyses. The concentration of the LCS is within the working range of the analytical method and does not require extensive pretreatment, dilution, or concentration prior to analysis. LCS samples are usually natural matrix materials to provide the best assessment of accuracy. The sources include, but are not limited to: QC samples, USGS-SRWS, EPA, commercially prepared samples, or samples prepared in-house with different sources than those used in the calibration standards. Recovery data from the LCS are compared to the control limits which are established for those analytes monitored by the LCS. Before any data can be accepted, the analytes of interest must fall within their expected control limits. If, for any reason, the results fall outside those limits, the sample results are unacceptable. A series of 5 to 8 LCSs are analyzed with each batch of samples at a frequency of about 30 % of the total number of samples in the batch..

Internal Standards

An internal standard is required for the quantitation of trace elements by inductively coupled plasma-mass spectrometry. The internal standard is similar in analytical behavior to the elements of interest and is added to all samples, standards, and blanks. Usually, more than one internal standard is added to each sample to evaluate the measurement of the sample throughout the entire time of analysis. Internal standards are used to compensate for instrument drift during the analysis. The internal standards determine the individual response factors used to calculate the concentrations of the elements of interest.

$$RF = (I_s)(C_{is})/(I_{is})(C_s)$$

where:

I_s = Intensity for reference analyte to be measured

I_{is} = Intensity for the internal standard

C_{is} = Concentration of the internal standard (μg/L)

C_s = Concentration of the reference analyte to be measured (μg/L)

$$C_s = (I_s/I_{is})(C_{is}/RF)$$

where:

C_a = Concentration of the analyte in sample in μg/L

I_a = Peak area of the analyte

RF = Response Factor

Sample Replicates

Replicates are environmental samples divided into three separate aliquots analyzed independently to determine the repeatability or precision of the analytical determination. The range or standard deviation in the replicate results must be within established control limits to ensure the generated data meet the quality assurance objectives for the particular analytical method.

Matrix Spike/Matrix Spike Duplicates

When necessary, a spiked environmental sample is used to check for any matrix effects on the precision and accuracy of an analytical measurement. When appropriate, one out of every 20 samples or one per batch is spiked with a known concentration of the analyte of interest, then analyzed in a normal manner. The percent recovery and relative percent difference are calculated and the results must fall within established control limits to ensure the generated data meets the QA objectives for the particular analytical method used.

Performance Evaluation Samples

PE samples are routinely used to the analyst to monitor both the analyst's work and analytical procedure. The recorded results are reviewed by laboratory senior staff. If any problems occur, follow-up corrective action is taken. PE samples may be in the form of blanks, previously analyzed environmental samples, split samples, or standard reference materials such as EPA, USGS, etc. Performance evaluation samples consist of at least 20 – 30 % of the total number of samples being analyzed.

Standard Method of Additions

Standard method of additions is the practice of adding known concentrations of analyte to a sample so that matrix effects (interferences) are minimized. Whenever sample interference is suspected, the method of standard additions is employed to verify the quality of the data.

Bracketing

Where appropriate, bracketing is use of standards to bracket the apparent concentration of the analyte in the sample. The sample is bracketed between a high and low standard, the standards being as close to the measured sample value as possible. The calculated results are then done by interpolation as follows:

$$C_s = [((I_s - I_{ls})(C_{hs} - C_{ls})/(I_{hs} - I_{ls})) + C_{ls}](\text{dilution})$$

where:

C_s = Sample Analyte Concentration

I_s = Intensity of Analyte in Sample

I_{hs} = Intensity of High Standard

I_{ls} = Intensity of Low Standard

C_{hs} = Concentration of High Standard

C_{ls} = Concentration of Low Standard

Normally, bracketing is used where precision of the methodology is poor. By bracketing, verification of data quality can be obtained.

9. Performance and System Audits

Performance and System Audits are an essential part of QA to ensure that the laboratory is statistically generating consistent valid data. A system audit consists of reviewing laboratory conditions, practices, equipment, staff, and procedures used to generate quality data. Performance audits verify the ability of the laboratory to correctly identify and quantitate analytes in blind check samples. The laboratory currently participates in several ongoing auditing programs on a regular basis. The audits can be categorized into external and internal audits.

External Audits

The laboratory participates in the following external audit programs:

- *U.S.G.S. Standard Reference Water Sample Program,* U.S. Geological Survey

- *Ecosystem Proficiency Testing QA Program*, Trace Elements in Surface Waters National Laboratory for Environmental Testing, National Water Research Institute, Environment Canada
- Split sample analysis with other laboratories both public and private

Internal Audits

Periodic audits using an in-house blind reference sample are conducted for specific routine procedures. The results of these analyses are evaluated by the Project Chief. System audits are conducted to assess the QA implementation in the laboratory. Inspection of QC charts, analytical procedures, equipment logs, and QA documentation in general is evaluated and reviewed for compliance and any needed operational changes. In addition, informal audits are conducted by the Project Chief as required when accuracy and precision of analyses appear to be drifting out of control. These audits may include the use of QC samples, varied matrices, calibration of instruments, and observation of the analyst to identify additional training or clarification needs, and may require changes in the analytical method. The control limits calculated for the Range (replicates) and Percent Recovery (Spikes) are based on the following equations:

Range

$$\overline{R} = |A - B|$$

$$\overline{R} = \frac{\left(\sum R\right)}{n}$$

when n = minimum of 20 duplicate pairs

$$\text{Upper control limit, UCL} = 3.327\,\overline{R}$$

$$\text{Warning Limit} = 2.456\,\overline{R}$$

Percent Recovery

%R = ((sample + spike) – sample x 100)/spike

n = minimum of 20 spike percent recoveries

x = (Σ%Rec)/n

$$\text{Std. deviation } (s_d) = \sqrt{\frac{n\left(\sum x^2\right) - \left(\sum x\right)^2}{n(n-1)}}$$

Upper Control Limit, UCL = $x + 3s_d$
Lower Control Limit, LCL = $x - 3s_d$

Upper Warning Limit, UWL = $x + 1.5s_d$
Lower Warning Limit, LWL = $x - 1.5s_d$

10. Preventive Maintenance

Preventive maintenance is routinely performed on all analytical equipment and instruments to minimize the amount of downtime and to maintain data quality. Equipment manuals, troubleshooting guides, and log books are available for maintenance support. Critical spare parts are kept on hand for laboratory instrumentation that is routinely repaired by laboratory staff. This inventory is monitored and maintained to avoid extended periods of downtime.

General Maintenance

Instrument operators are responsible for routine daily maintenance such as cleaning external optics, making adjustments in focus, cleaning sampler probes, etc. and for maintaining the equipment log books. Designated laboratory personnel are trained and responsible for more complex maintenance procedures. All necessary repairs are performed by trained staff or factory service engineers. The Project Chief will be informed of the need for, and the performance of, all major maintenance activities, where these activities may directly impact sample analysis schedules.

Equipment Log Books

Equipment log books are maintained for all analytical instruments and equipment used in the laboratory. Each entry in the log book includes the date, the nature of the entry, and the name of the individual responsible for the entry. The following information is recorded in the log books:

- Results of all sensitivity checks (verifying the equipment is operating according to QA criteria for the method and/or meets the manufacturer's specifications)
- All scheduled maintenance performed
- Any major or minor problem encountered, a brief description, corrective action required, and a list of any parts replaced
- Verification of equipment operation after any maintenance is performed by designated laboratory staff

The equipment log books are periodically reviewed for compliance and problem areas in the equipment by the Project Chief.

11. Routine Procedures Used to Assess Data Quality

The effectiveness of data quality assessment in a QA program is measured by the quality of data generated by the laboratory. Data quality is evaluated in terms of precision, accuracy, comparability, and completeness.

Precision and Accuracy

Precision is the degree to which the measurement is reproducible among replicate observations, and accuracy is a determination of how close the measurement is to the true value. Laboratory precision and accuracy have been established for all analytical procedures used and are assessed for each sample set that is analyzed. The precision of analytical data is determined routinely by running triplicate tests on samples, laboratory control standards, and matrix spikes within the sample set. Accuracy is evaluated by analysis of natural matrix standard reference materials, or secondary reference materials traceable to the National Institute of Standards and Technology and to a lesser extent by the analysis of spiked samples. Sample spikes are prepared by addition of a known amount of analyte to a sample. The spiked sample and unspiked sample are then analyzed for the parameter of interest. Precision and accuracy assessment utilize control charts and well established statistical procedures found in the following reference publications:

- ***Handbook for Analytical Quality Control in Water and Wastewater Laboratories*** (EPA 600/4-79-019, March 1979)
- ***Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments***, Techniques of Water Resources Investigations, USGS, Book 5, Chapter A6, 1982

Comparability

Comparability expresses the confidence with which the data set can be compared to other data sets measuring the same properties. See Section 7. Data Validation and Reporting, for procedures used to evaluate comparability for assessment of data quality.

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount expected to be obtained under normal conditions. For data quality assessment procedures used to evaluate the completeness of data, see Section 7. Data Validation and Reporting.

Detection Limits

The sensitivity of any analytical method is related to the detection limits, the lowest concentration of analyte that can be detected at a specified confidence level. Definitions of Instrument Detection Limit, Method Detection Limit, Method Quantification Limit, and Practical Quantification Limit follow:

Instrument Detection Limit

Definition: The smallest signal above background noise that the instrument can detect reliably at 99 percent confidence level.
Measurement: Analyze replicate blank samples to determine the extent which the analyte signal exceeds the peak-to-peak noise.
Calculation: The mean value plus two standard deviations for a normal distribution or three for data distribution. (See Skogerboe and Grant, 1970). Detection limits are usually reported as less than (>) values in the data set.

Method Detection Limit

Definition: The lowest possible concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing analyte.
Measurement: Analyze several replicates of a sample, digestate, or extracted sample with no detectable analyte to establish the estimated MDL. Prepare a concentration between three to five times the estimated MDL. Analyze seven aliquots and process each through the entire analytical method then calculate the standard deviation.

$$s_d = \sqrt{\frac{n\left(\sum x^2\right) - \left(\sum x\right)^2}{n(n-1)}}$$

Calculation: (S_d)
From a table of the one-sided (t) distribution select the value of (t) for 7-1=6 degrees of freedom at the 99 percent level; this value is 3.143. The following relationship is used to calculate the MDL: MDL = 3.143 (S_d)

Practical Quantification Limit

Definition: The minimum level that can be reliably achieved by the analytical method within specified limits of precision and accuracy during routine laboratory operating conditions.
Measurement: The PQL is 5 to 10 times the MDL.

Reporting Limits
The reporting limit is the PQL value of the specific analytical method.

12. Corrective Action

When errors, deficiencies, or out of control conditions are encountered, corrective actions are necessary. The need for corrective action may be identified in any number of ways:

- C data outside acceptable limits for a given sample set
- Rising or falling trends that are detected in Standard Reference Materials or spike recovery or duplicate control charts
- Unacceptable levels of contamination in blanks and reagents
- Unusual changes in detection limits
- Calibration standards with low sensitivity
- Nonlinear or misshapen calibration curves
- Deficiencies detected by Project Chief or senior staff reviewing analytical data
- Deficiencies detected during internal or external audits by Project Chief, outside agency, or from performance evaluation studies

Since each analytical method has a QA Section that outlines corrective actions to be taken, problems which may arise are usually handled at the analyst's level. If the problem persists and cannot be handled by the analyst, the matter is referred to the Project Chief. The following corrective action steps are then taken:

- Identification of the problem
- Investigation and determination of the cause of the problem
- Corrective action determined to eliminate the problem
- Assigning responsibility for implementing corrective action
- Evaluation of the effectiveness of the corrective action
- Verification that the corrective action has eliminated the problem
- Documentation of the problem and corrective action needed

All suspect analytical results will be evaluated. The Project Chief will not permit the analysis to go on-line until the corrective action has been completely successful. Corrective action documentation is routinely reviewed by the Project Chief

for recurring problems which may require changes in analytical procedures, methods, or additional training of analysts.

13. Quality Assurance Reports

QA Reports are generated by the Staff Scientists with assistance from senior staff. These reports are used in evaluating the overall QA Program, identifying problems and trends, and planning for future needs and requirements. These reports will usually include the following:

- All audit results including any necessary corrective action required
- Performance evaluation results and commentary
- Problems encountered and corrective action taken
- Any significant QA problems encountered
- Comments and recommendations

External reference samples from USGS, USEPA, and approved outside organizations are analyzed several times per year. A QA report is generated after each external reference is completed. If special problems arise involving more than normal corrective action, a special QA Report will be issued. The reports will be routed to specific staff members and finally, the Project Chief.

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APPENDIX C

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

FOR THE USGS

WATER, ENERGY, AND BIOGEOCHEMICAL BUDGETS (WEBB)

PROJECT LABORATORY

COLORADO DISTRICT, LAKEWOOD, CO

FEBRUARY, 2003

METHOD REPORTING LIMITS

2002 Method Detection Limits (MDL) and Laboratory Reporting Limits (LRL) for WEBB laboratory

Constituent	Method	LT-MDL	LRL	Units
Cl	IC	0.5	1.0	µeq/L
NO3	IC	0.2	0.4	µeq/L
SO4	IC	0.3	0.6	µeq/L
K	IC	0.2	0.4	µeq/L
Na	IC	0.2	0.4	µeq/L
NH4	IC	0.5	1.0	µeq/L
DOC	IR	0.2	0.4	mg/L
SC	Wheatstone Bridge	0.5	1.0	µS/cm
Ca	ICP	1.7	3.4	µeq/L
Mg	ICP	0.7	1.3	µeq/L
Na	ICP	0.9	1.8	µeq/L
SiO2	ICP	2.0	3.9	µeq/L
Sr	ICP	0.009	0.018	µeq/L
K	ICP	0.5	1.0	µeq/L

LABORATORY CUSTODY

Physical Custody and Log-In

Upon arrival in the laboratory, all samples are placed in the sample storage refrigerator until they can be logged into the master chemical database. Log-in typically takes place on the day of sample arrival or the following working day at the latest. All unpreserved sample aliquots (FU, RU, and DOC) are refrigerated until all analyses are completed. Samples are stored separately from laboratory solutions.

Sample Tracking

The database automatically updates the sample ID number assigned to each sample as it is logged-in. This ID number is unique and follows each sample with all of its subsets as a permanent record. Information necessary to complete the log-in procedure includes:

sample type
site
collection date
collection time
stage, ground water depth or precipitation volume
water temperature
field comments

After entry into the database the program software will begin the sample tracking process which provides the status of each sample. Unless superseded by the project chief, senior research personnel, or other principle investigator samples are analyzed in the order in which they are logged in.

Samples are tracked in the database by analysis date. When a sample is logged-in, all analysis dates are set to "00/00/00". A status report shows the number of samples pending and the first ID number for all parameter groups in the laboratory. As analysts request worksheets from the database the analysis date for that parameter group is set to the current date. This analysis date may be edited when data is entered or uploaded if that workload is not completed on the original date.

Completed data is either entered manually or uploaded electronically to the database. Before any data are uploaded to the database a "Z" score report is generated from the standard references run with those samples. Standard references must fall within expected limits before these data are accepted and uploaded; or those samples are returned to the database for reanalysis. When all data is completed for a sample the ion balance and conductivity balance are calculated. These balances are evaluated by the lab manager for acceptance or for sample rerun. When all data have been accepted that sample is removed from active storage and is archived permanently in the warehouse.

ANALYTICAL PROCEDURES

Laboratory Glassware Cleaning and Storage

Cleaning procedures for glass and plasticware are as follows: glass and plasticware are washed with a phosphate-free detergent then triple rinsed with 18 megaohm deionized water and air dried. Glass and plasticware are stored either in the large cabinet or in designated lab drawers and cabinets.

Laboratory Reagent and Standard Storage

Chemical Type	Method of storage
Inorganic acids	Stored in original containers in a vented cabinet designed for the storage of inorganic acids.
Organic Acids	Stored in original containers in a vented cabinet designed for the storage of organic acids.
Inorganic salts	Stored in original containers on laboratory shelving assigned for the storage of inorganic salts. Note: oxidizers are stored separately.
Organic salts	Stored in original containers on laboratory shelving assigned for the storage of organic salts.
Oxidizing salts	Stored in original containers in a vented cabinet designed for the storage of oxidizers.
Flammable solvents	Stored in original containers in a vented cabinet designed for the storage of flammable liquids.
Organic solvents	Stored in original containers in a vented cabinet designed for the storage of organic solvents.
Compressed gases	stored in vendor cylinders in a fenced in area of the warehouse. Note: in the laboratory all cylinders are secured using a strapping device.
Metals Standards	Stored in original containers in designated laboratory cabinets.

Note: all original containers are marked with the date of receipt and date opened.

Laboratory Instrument Calibration Procedures

If method calibration procedures exceed the calibration requirements listed below, they will take precedence. All instrument or equipment calibration results must be recorded in the appropriate instrument or equipment calibration log. All standards are made from ACS grade, other high purity designated reagent salts or commercially prepared stock solutions that are traceable to NIST.

Specific Conductance Meter

Basic calibration of instruments is performed in accordance with manufacturer's instructions. Standards used for calibration are prepared from a stock KCl solutuion. The temperature of standards and water samples should be at or near room temperature.

Sequence of events.

a. Initial calibration. The probe is rinsed with DI then with the standard to be read. Pour a fresh aliquot of standard and immerse the probe. Adjust the meter to read the correct value. Repeat with the second standard.

b. Check standard reference water sample-Must be within ±2.0 standard deviations of the expected value to accept initial calibration.

c. Verify intermediate standard-Must be within ±2.0 standard deviations of the expected value to continue.

d. If intermediate standard or QA check standard fails criteria, analysis must be stopped, initial calibration repeated (steps a - c), and samples prior to failed check reanalyzed.

pH Meter

Basic calibration of instruments is performed in accordance with manufacturer's instructions. Initial calibration is a 2 point standard curve over the expected operating range, performed at least once a day and on the failure of any intermediate standard. Standards used for calibration are obtained from commercial sources. The temperature of buffers and water samples should be at or near room temperature.

Sequence of events.

a. Initial calibration The probe is rinsed with DI then with the pH 7.0 buffer. Pour a fresh aliquot of standard and immerse the probe. Adjust the meter to read the correct value. Repeat with the second buffer.

b. Check standard reference water sample-Must be within ±2.0 standard deviations of expected value to accept initial calibration.

c. Verify intermediate standard-Must be within ±2.0 standard deviations of the expected value to continue.

d. If intermediate standard or QA check standard fails criteria, analysis must be stopped, initial calibration repeated (steps a - c), and samples prior to failed check reanalyzed.

Alkalinity Auto-Titrator

Basic calibration of instruments is performed in accordance with manufacturer's instructions. Since the sensing element in this auto-titrator is a pH probe, the calibration sequence for pH meters is followed. Initial calibration is a 2 point standard curve over the expected operating range, performed at least once a day and on the failure of a QA check standard. Standards used for calibration are obtained from commercial sources. The temperature of buffers and water samples should be at or near room temperature.

Sequence of events.

a. Initial calibration The titrator is calibrated using the manufacturers calibration software. Pour buffers and DI into respective sample cups.

b. The sample wheel should be loaded with a blank and standard at the beginning, a duplicate at the midpoint, and 2 SRWS at the end. QA check standards must be within ±2.0 standard deviations of the expected values, or the run queue must be reanalyzed.

Ion Chromatography (IC)

The ion chromatograph is set up according to the manufacturer's specifications. For each run the initial calibration for each solute is determined from a six- or seven-point standard curve The system is recalibrated on the failure of any intermediate standard. All curves are checked by the analyst to assure a correlation coefficient of 0.995 or higher.

Sequence of events.

a. Initial calibration. Run six mixed-solute standards for the anion system and seven mixed-solute standards for the cation system

b. Check calibration standards against the last run calibration; standard results should not differ by more than 5%. Evaluate the linearity of the new calibration curve and determine acceptance/rejection (r^2 better than 0.995).

c. If the initial calibration is rejected, rerun the standards; if rejected again, remake the working standards and repeat steps a & b.

d. Run 3 working standards and at least three standard-reference water samples (SRWS) in the expected sample concentration range. The solute determinations for the SRWS must be within ±2.0 standard deviations (determined on long-term

analyses of the SRWS at our laboratory) of the expected value to accept initial calibration.

e. Verify 3 intermediate standard, which must be within 5% of the expected value to continue.

f. Analyze 17 samples (includes reagent blanks and duplicates).

g. Re-verify with blank and 3 SRWS. Must be within ±2.0 standard deviations for SRWS.

h. Continue steps f and g for the entire run and end the run with the SRWS used at the beginning of the run.

i. If intermediate standard or QA check standard fails criteria, analysis is interrupted, initial calibration repeated (steps a - c), and samples prior to failed check reanalyzed.

Inductively Coupled Plasma Spectroscopy (ICP)

The inductively coupled plasma spectrometer is set up according to the manufacturer's specifications. For each run the initial calibration for each solute is a five-point standard curve. The system is recalibrated on the failure of an intermediate standard. All curves are checked by the analyst to assure a correlation coefficient of >0.995.

Sequence of events.

a. Initial calibration. Use five mixed-solute standards to calibrate the system.

b. Evaluate the linearity of the new calibration curve and determine acceptance/rejection.

c. If the initial calibration is rejected, rerun the standards; if rejected again, remake the working standards and repeat steps a & b.

d. Run at least two standard-reference water samples (SRWS) in the expected sample concentration range. These SRWS must be within 2.0 standard deviations to accept initial calibration.

e. Verify intermediate standard, which must be within 5% of the expected value to continue.

f. Analyze ten samples (includes reagent blanks, spikes, and duplicates).

g. Re-verify intermediate standard or SRWS. Must be within 5% for intermediate standard or 1.5 standard deviations for SRWS.

h. Continue steps f and g for the entire run and end the run with the SRWS used at the beginning of the run.

i. If intermediate standard or QA check standard fails criteria, analysis is interrupted, initial calibration repeated (steps a - c), and samples prior to failed check reanalyzed.

Laboratory Equipment

Equipment Type	Manufacturer's Name	Model Number	Age
Titration System	Radiometer	TIM900	1
Balance	Mettler	AG245	4
ICP	Perkin-Elmer DV ICP-AES	Optima 3300	1
Specific Conductance	YSI	Model 32	8
pH Meter	Orion	Model 120	4
Ion Chromatograph	Dionex	DX120	1

Laboratory Equipment Monitoring

The records of all equipment and instrument monitoring are recorded in a laboratory equipment/instrument log. Entries include at least the following information.

1. The results of each performance/calibration check.

2. Date and time of check.

3. Initials of person(s) making check.

4. Proper description of equipment or instrument checked and all test equipment used in making check.

5. All appropriate comments concerning operating conditions.

Reagent Water System

a. The output water from the ion-exchange cartridge system is monitored continuously. If the DI exceeds 0.5 µS, no reagents or standards are prepared until the cartridges are replaced.

Standard and Reagent Documentation

All reagents and standards prepared in-house have the following documentation affixed to the container which also is recorded in the log by the workgroup using that material.

a. Date prepared

b. Concentration of reagent or standard.

c. Initials of preparer.

Quality Control Checks

Water used to prepare blanks and check samples is analyte-free for the specific analytes to be analyzed. If method or project QA/QC requirements exceed the requirements as outlined below, they take precedence.

Each laboratory analytical set of samples is required to contain a minimum of the following:

1. One method reagent blank.

2. Quality control samples (SRWS) at the rate of one per ten samples.

3. Quality control check standards at the rate of one per ten samples.

4. Sample duplicates at the rate of one per twenty samples.

Control Charts

Standard reference data are entered into the analytical database along with the sample data and analysis dates. QA/QC charts are developed and the standard reference data are reviewed before any data is accepted and appended to the database. An example of typical control charts for IC anions are included at the back of this section.

Method Detection Limit (MDL)

The MDL for any laboratory procedure are developed in the following manner. Blank water is analyzed several times in each run according to laboratory procedure The standard deviation for each solute is calculated and MDL is calculated as the standard deviation of the blanks times the students t distribution. The MDL is updated or verified annually and these results are recorded in the respective laboratory notebook.

DATA REDUCTION, VALIDATION AND REPORTING

Data Reduction

The laboratory analyst is responsible for converting all raw values produced in the laboratory into reportable data. The records of all reduction calculations are kept in

respective laboratory notebooks. All computer printouts, chromatograms, and strip charts are labeled, dated, and initialed by the analyst performing the analysis. These hardcopies are archived for the life of the project.

Each laboratory worksheet shows the sample ID number and the parameters to be run. All anions by IC are calculated by *Peak Net* computer software using polynomial regression. All metals by ICP are calculated by an visual basic program written in Excel.

Data Quality

a) Integrity

The laboratory manager is responsible for checking all data entries, calculations, calibration integrity, and instrument logs.

b) Validation

Method reagent blanks are checked by the analyst at the time of analysis to insure that they do not exceed the MDL. Quality control samples are checked by the analyst at the time of analysis to insure that the reported value for each analyte is within 2.0 standard deviations of the documented most probable value for that reference sample. Matrix spikes are checked by the analyst to insure that recovery is at least 90-110%. Duplicate samples are checked by the analyst to insure that values replicate within 10%.

Data Reporting

The final data report is generated by computer. This report shows the recovery of all quality control samples within a data set pending entry versus the historical mean those analytes. This report is presented to the laboratory manager, who is ultimately responsible for approving all data for acceptance. An example of a typical run queue and final data report is included at the back of this section.

Data Storage

All laboratory worksheets, notebooks, and logbooks are considered original data and are retained permanently. In addition to the paper records, the laboratory manager maintains a computerized database containing all sample login information and the results of all chemical analyses performed in the laboratory. Weekly incremental magnetic tape backups are made of these files. All data are maintained on-line for easy computer retrieval.

Corrective Action

The analyst performing the analysis is responsible initiating corrective action if any of the QA checks do not meet stated acceptance criteria. The laboratory manager does routine checks to insure that these QA checks are being performed and that proper corrective action is taken when necessary.

A QA reference sample or blind reference sample which exceeds acceptance criteria causes a subset of samples to be reanalyzed. These samples, which are to be reanalyzed, begin with the last QA reference sample that was in control and end with the following QA reference sample. Other sample data in that data set are considered to be unaffected up to the point of the sample which exceeded acceptance criteria and are entered into the master chemical database Affected sample data are not entered into the master chemical database.

PERFORMANCE AND SYSTEM AUDITS

Internal Laboratory System Audits

The District Safety Officer conducts routine safety inspections of the laboratory The Safety Officer reports any inadequacies to the laboratory manager and project chief.

The laboratory manager reviews the laboratory annually. This review consists of a detailed inspection of:

1. Sample management system.
2. Conformance of laboratory operations to QA/QC plan.
3. Analytical methodologies used.
4. Standard operating procedures of the laboratory.
5. Records including instrument or workgroup notebooks and quality control charts.
6. Use of reference materials and other quality assurance samples in the laboratory.
7. Quality control checks used to verify adequacy of completed analysis.
8. Data entry and data review procedures.
9. External evaluation programs in which the laboratory participates and results from these studies.

The laboratory manager prepares a written report of significant findings for the project chief. If deficiencies are found, the laboratory manager prepares a corrective action program and submits this program to the project chief for approval. Upon approval the corrective action program is instituted by the laboratory manager.

External Laboratory Performance Audits

Standard Reference Water Sample (SRWS) Program

Participation in this continuing quality-assurance program is mandatory for all laboratories providing water-quality data for U.S. Geological Survey use. A major constituent, trace metal constituent, precipitation, and nutrient sample are prepared by BQA and distributed to laboratories twice a year. Natural waters are used to prepare these samples and maybe spiked with varying analytes to provide increase the range in concentration. Our laboratory has participated in this program since 1995. We analyze only the precipitation and nutrient samples due to the dilute nature of the environmental samples typically analyzed in our laboratory.

NIVA

The USGS WEBB project laboratory voluntarily participates in an ongoing laboratory intercomparison study conducted by the Norwegian Institute for Water Research (NIVA). Two samples of natural waters are sent to participating laboratories each year by the NIVA. Samples are analyzed for major cations and anions, silica, alkalinity, pH, specific conductance, and dissolved organic carbon. Results are reported by the NIVA in annual reports (see accompanying table).

DOC Round Robin

The USGS WEBB project laboratory participates in a dissolved organic carbon (DOC) laboratory intercomparison study conducted by the USGS/NRP in Boulder, Colorado. Ten DOC natural water samples are sent to participating laboratories during each round-robin. Results available upon request.

Quality Assurance Reports

Annual QA reports are generated by the database management system showing ion balances and time series plots for all the samples analyzed during the year. A copy of this report is distributed to all project staff.